Vibronic coupling density and related concepts

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Abstract. Vibronic coupling density is derived from a general point of view as a one-electron property density. Related concepts as well as their applications are presented. Linear and non-linear vibronic coupling density and related concepts, orbital vibronic coupling density, reduced vibronic coupling density, atomic vibronic coupling constant, and effective vibronic coupling density, illustrate the origin of vibronic couplings and enable us to design novel functional molecules or to elucidate chemical reactions. Transition dipole moment density is defined as an example of the one-electron property density. Vibronic coupling density and transition dipole moment density open a way to design light-emitting molecules with high efficiency.

1. Introduction
Vibronic couplings\textsuperscript{[1, 2, 3]} give rise to Jahn-Teller effect in a degenerate state, reorganization energy in an ionized state, and non-radiative decay and vibrational relaxation in an excited state. Vibronic couplings have been investigated in density forms\textsuperscript{[4, 5]}. The spatial integral of the density form, vibronic coupling density (VCD), yields a vibronic coupling constant (VCC). Thus, the distribution of a VCD provides an insight into the magnitude of a VCC. Moreover, the vibronic interaction can be analyzed on the basis of the electronic and vibrational structures by using the VCD concept, since the VCD can be decomposed as the product of an electron density/overlap density and a potential derivative.

The VCD concept has been applied for the designs of carrier-transporting molecules \textsuperscript{[6, 7, 8]}, analyses of inelastic tunneling spectroscopy\textsuperscript{[9]}, Jahn-Teller couplings in C\textsubscript{60}\textsuperscript{[10]}, electron-vibration coupling in hydrocarbons \textsuperscript{[4, 11]}, and vibronic progression in the spectrum of an organic molecule\textsuperscript{[12]}.

In this article, we derive vibronic coupling densities from a general point of view, one-electron property density. We propose transition dipole moment density as other example of the one-electron property density. We summarize related concepts to VCD, orbital vibronic coupling density, reduced vibronic coupling density, atomic vibronic coupling constant, and effective vibronic coupling density. We present some illustrative examples of their applications. In Sec. 2, we define vibronic couplings, and they are expressed in density forms in Sec.3 as a one-electron property density. In Sec.4, we define transition dipole moment density. We summarize related concepts to VCD in Sec. 5. Their applications are presented in Sec. 6. We summarize these results in Sec.7.
2. Vibronic Coupling Densities

We regard a stationary geometry $R_0$ for an electronic state $\Psi_0$ as a reference system. A molecular Hamiltonian, $\hat{H} = \hat{T}_e + \hat{U}_{ee} + \hat{U}_{en} + \hat{U}_{nn}$ where $\hat{T}_e$ denotes kinetic operator of electrons, $\hat{U}_{ee}$ electron-electron potential, $\hat{U}_{en}$ electron-nucleus potential, $\hat{U}_{nn}$ nucleus-nucleus potential, is expanded as the Hertzberg-Teller series in terms of a normal coordinate $Q_\alpha$ around the reference geometry $R_0$:

\[
\hat{H}(\{Q_\alpha\}) = \hat{H}(0) + \sum_\alpha \left( \frac{\partial \hat{H}}{\partial Q_\alpha} \right)_{R_0} Q_\alpha + \frac{1}{2} \sum_{\alpha,\beta} \left( \frac{\partial^2 \hat{H}}{\partial Q_\alpha \partial Q_\beta} \right)_{R_0} Q_\alpha Q_\beta \\
+ \cdots + \frac{1}{n!} \sum_{\alpha_1, \ldots, \alpha_n} \left( \frac{\partial^n \hat{H}}{\partial Q_{\alpha_1} \cdots \partial Q_{\alpha_n}} \right)_{R_0} Q_{\alpha_1} \cdots Q_{\alpha_n} + \cdots \tag{1}
\]

\[
= \hat{H}(0) + \sum_\alpha \hat{V}_\alpha Q_\alpha + \frac{1}{2} \sum_{\alpha,\beta} \hat{W}_{\alpha\beta} Q_\alpha Q_\beta + \cdots \\
+ \frac{1}{n!} \sum_{\alpha_1, \ldots, \alpha_n} \hat{W}^{(n)}_{\alpha_1 \cdots \alpha_n} Q_{\alpha_1} \cdots Q_{\alpha_n} + \cdots, \tag{2}
\]

where

\[
\hat{V}_\alpha = \left( \frac{\partial \hat{H}}{\partial Q_\alpha} \right)_{R_0}
\]

is the electronic part of a linear vibronic coupling,

\[
\hat{W}_{\alpha\beta} = \left( \frac{\partial^2 \hat{H}}{\partial Q_\alpha \partial Q_\beta} \right)_{R_0}
\]

is the electronic part of a quadratic vibronic coupling, and

\[
\hat{W}^{(n)}_{\alpha_1 \cdots \alpha_n} = \left( \frac{\partial^n \hat{H}}{\partial Q_{\alpha_1} \cdots \partial Q_{\alpha_n}} \right)_{R_0}
\]

is the electronic part of an $n^{th}$ vibronic coupling. Note that $\hat{W}^{(1)}_\alpha = \hat{V}_\alpha$ and $\hat{W}^{(2)}_{\alpha\beta} = \hat{W}_{\alpha\beta}$.

The nuclear-electronic attractive potential $\hat{U}_{en}$ is written as

\[
\hat{U}_{en} = \sum_i u(r_i), \tag{6}
\]

where $r_i$ is the position of electron $i$, and

\[
u(r_i) = -\sum_A \frac{Z_A e^2}{|r_i - R_A|} \tag{7}
\]

is the potential from nuclei $A$ with the position $R_A$ and the charge $Z_A$ acting on a single electron.

The nuclear-nuclear repulsive potential $U_{nn}$ is written as

\[
U_{nn} = \sum_{A,B} \frac{Z_A Z_B e^2}{|R_B - R_A|}, \tag{8}
\]
The $n^{th}$ order derivative of potential $u$ with respect to $Q_{\alpha_1}, \cdots, Q_{\alpha_n}$ is denoted by

$$\hat{w}_{\alpha_1,\cdots,\alpha_n}^{(n)}(\mathbf{r}) := \left( \frac{\partial^n u(\mathbf{r})}{\partial Q_{\alpha_1} \cdots \partial Q_{\alpha_n}} \right)_{\mathbf{R}_0}. $$

(9)

For the linear and quadratic derivative, we define

$$\hat{v}_{\alpha}(\mathbf{r}) := \hat{w}_{\alpha}^{(1)}(\mathbf{r}) = \left( \frac{\partial u(\mathbf{r})}{\partial Q_{\alpha}} \right)_{\mathbf{R}_0} $$

(10)

and

$$\hat{w}_{\alpha\beta}(\mathbf{r}) := \hat{w}_{\alpha\beta}^{(2)}(\mathbf{r}) = \left( \frac{\partial^2 u(\mathbf{r})}{\partial Q_{\alpha} \partial Q_{\beta}} \right)_{\mathbf{R}_0}. $$

(11)

respectively. The vibronic operators can be decomposed as follows:

$$\hat{V}_{\alpha} = \sum_i \hat{v}_{\alpha}(\mathbf{r}_i) + \left( \frac{\partial U_{\alpha\alpha}}{\partial Q_{\alpha}} \right)_{\mathbf{R}_0}, $$

(12)

$$\hat{W}_{\alpha\beta} = \sum_i \hat{w}_{\alpha\beta}(\mathbf{r}_i) + \left( \frac{\partial^2 U_{\alpha\alpha}}{\partial Q_{\alpha} \partial Q_{\beta}} \right)_{\mathbf{R}_0}, $$

(13)

$$\hat{W}_{\alpha_1,\cdots,\alpha_n}^{(n)} = \sum_i \hat{w}_{\alpha_1,\cdots,\alpha_n}^{(n)}(\mathbf{r}_i) + \left( \frac{\partial^n U_{\alpha\alpha}}{\partial Q_{\alpha_1} \cdots \partial Q_{\alpha_n}} \right)_{\mathbf{R}_0}. $$

(14)

It should be noted that the vibronic coupling operators consist of a sum of the one-electron operators, $\hat{v}_{\alpha}$, $\hat{w}_{\alpha\beta}$, and $\hat{w}_{\alpha_1,\cdots,\alpha_n}^{(n)}$, respectively.

The linear vibronic-coupling matrix is defined as

$$(\mathbf{V}_{\alpha})_{lm} = \left\langle \Psi_l \left| \hat{V}_{\alpha} \right| \Psi_m \right\rangle, $$

(15)

where $\Psi_l$ and $\Psi_m$ are electronic wavefunctions at the reference geometry $\mathbf{R}_0$. We simply call a diagonal element of the linear vibronic-coupling matrix as a vibronic coupling constant (VCC) $V_{\alpha}$ hereafter. The quadratic vibronic-coupling matrix is defined as

$$(\mathbf{W}_{\alpha\beta})_{lm} = \left\langle \Psi_l \left| \hat{W}_{\alpha\beta} \right| \Psi_m \right\rangle, $$

(16)

and the $n^{th}$ order vibronic-coupling matrix is defined as

$$(\mathbf{W}_{\alpha_1,\cdots,\alpha_n}^{(n)})_{lm} = \left\langle \Psi_l \left| \hat{W}_{\alpha_1,\cdots,\alpha_n}^{(n)} \right| \Psi_m \right\rangle. $$

(17)

We simply call a diagonal element of the quadratic vibronic-coupling matrix as a quadratic vibronic-coupling constant (QVCC) $W_{\alpha\beta}$ hereafter.

The diagonal linear vibronic coupling density, which is simply called as a vibronic coupling density (VCD), is defined as

$$\eta_{\alpha}(\mathbf{r}) = \Delta \rho(\mathbf{r}) \times v_{\alpha}(\mathbf{r}), $$

(18)

where $\Delta \rho$ is an electron density difference between $\Psi$ and the reference electronic state $\Psi_0$. The integral of the VCD yields the VCC:

$$V_{\alpha} = \int \eta_{\alpha}(\mathbf{r}) d^3 \mathbf{r} = \int \Delta \rho(\mathbf{r}) \times v_{\alpha}(\mathbf{r}) d^3 \mathbf{r}. $$

(19)
This equation is proved in the following Section. From this equation, the VCC can be analyzed based on electronic and vibrational states.

For the \( n \)-th order coupling, vibronic coupling density between \( \Psi_k \) and \( \Psi_l \) is defined as

\[
\eta_{n}^{(n)}(\mathbf{r}) = \rho_{kl}(\mathbf{r}) \times \hat{\omega}_{n}^{(n)}(\mathbf{r}).
\]

\( \rho_{kl}(\mathbf{r}) \) is defined in the following Section. The diagonal matrix element of the \( n \)-th order vibronic-coupling matrix is written as

\[
(W_{\alpha_{1} \cdots \alpha_{n},kl}^{(n)})_{kk} = \int \rho_{k}(\mathbf{r}) \times \hat{\omega}_{\alpha_{1} \cdots \alpha_{n}}^{(n)}(\mathbf{r}) d^{3}r + \left( \frac{\partial^{n}U_{nn}}{\partial Q_{\alpha_{1}} \cdots \partial Q_{\alpha_{n}}} \right) R_{0},
\]

where \( \rho_{k} = \rho_{kk} \). The off-diagonal element is written as

\[
(W_{\alpha_{1} \cdots \alpha_{n},kl}^{(n)})_{kl} = \int \rho_{kl}(\mathbf{r}) \times \hat{\omega}_{\alpha_{1} \cdots \alpha_{n}}^{(n)}(\mathbf{r}) d^{3}r.
\]

For the quadratic coupling,

\[
\eta_{2}^{(2)}(\mathbf{r}) = \rho_{kl}(\mathbf{r}) \times \hat{\omega}_{\alpha_{1} \alpha_{2}}(\mathbf{r}).
\]

The QVCC is written as

\[
(W_{\alpha_{1} \alpha_{2}}^{(2)})_{kk} = \int \rho_{k}(\mathbf{r}) \times \hat{\omega}_{\alpha_{1} \alpha_{2}}(\mathbf{r}) d^{3}r + \left( \frac{\partial^{2}U_{nn}}{\partial Q_{\alpha_{1}} \partial Q_{\alpha_{2}}} \right) R_{0},
\]

and the off-diagonal QVCC

\[
(W_{\alpha_{1} \alpha_{2}})_{kl} = \int \rho_{kl}(\mathbf{r}) \times \hat{\omega}_{\alpha_{1} \alpha_{2}}(\mathbf{r}) d^{3}r.
\]

3. Vibronic Coupling Density as a One-Electron Property Density

We prove Eqs. (19), (21), (22), (24), and (25) from a general point of view, since the vibronic coupling operators are a one-electron operator. The proof for VCDs including non-linear VCDs have been already published[8]. The present proof is an extension as a one-electron operator. The electron density of the \( N \)-electron state \( \Psi_{k}(\mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) \) which can be either an ionized or an excited state is defined by

\[
\rho_{k}(\mathbf{r}) := N \int \Psi_{k}^{*}(\mathbf{r} s_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) \Psi_{k}(\mathbf{r} s_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) d\mathbf{s_{1}} d\mathbf{x}_{2} \cdots d\mathbf{x}_{N},
\]

where \( \mathbf{x}_{i} \) denotes space coordinate \( r_{i} \) and spin coordinate \( s_{i}[13] \).

The overlap density between the \( N \)-electron states, \( \Psi_{k}(\mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) \) and \( \Psi_{l}(\mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) \), is defined by

\[
\rho_{kl}(\mathbf{r}) := N \int \Psi_{k}^{*}(\mathbf{r} s_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) \Psi_{l}(\mathbf{r} s_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) d\mathbf{x}_{2} \cdots d\mathbf{x}_{N}.
\]

\[\rho_{kk}(\mathbf{r}) = \rho_{k}(\mathbf{r}).\]

From the antisymmetric principle for Fermions:

\[
\Psi_{k}(\mathbf{x}_{\sigma(1)}, \mathbf{x}_{\sigma(2)}, \cdots, \mathbf{x}_{\sigma(N)}) = \text{sgn} (\sigma) \Psi_{k}(\mathbf{r} s_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}),
\]
where $\sigma \in S_N$ ($n^{th}$ order symmetric group). The product of two electronic wavefunctions satisfies

$$\Psi_k^\dagger(x_{\sigma(1)}, \ldots, r_{s1}, \ldots, x_{\sigma(N)}) \Psi_l(x_{\sigma(1)}, \ldots, r_{s1}, \ldots, r_{\sigma(N)})$$

\[= (\text{sgn}(\sigma))^2 \Psi_k^\dagger(r_{s1}, x_2, \ldots, x_N) \Psi_l(r_{s1}, x_2, \ldots, x_N)\]

\[= \Psi_k^\dagger(r_{s1}, x_2, \ldots, x_N) \Psi_l(r_{s1}, x_2, \ldots, x_N).\] (30)

According to the antisymmetric principle of Fermions,

\[\Psi_k^\dagger(r_{s1}, x_2, \ldots, x_N) \Psi_l(r_{s1}, x_2, \ldots, x_N) = \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi_k^\dagger(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \Psi_l(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\]

\[= \frac{1}{N} \rho_{kl}(\mathbf{r}).\] (31)

This is also the case for the electron density $\rho_{kk}(\mathbf{r}) = \rho_k(\mathbf{r})$.

We consider a one-electron property $\hat{O}_1$ which is a sum of one-electron operators $\hat{o}_1$:

\[\hat{O}_1 = \sum_i \hat{o}_1(r_i).\] (32)

The vibronic coupling operators are such a one-electron property. An electric dipole moment operator is also a one-electron property operator. We will discuss a transition dipole moment which is regarded as an off-diagonal element of $\hat{\mu}$ as a density form in the following Section.

The matrix element of a one-electron operator $\hat{O}_1$ between $\Psi_k$ and $\Psi_l$ is written as

\[(\Omega_{kl})_{kl} = \left\langle \Psi_k \left| \hat{O}_1 \right| \Psi_l \right\rangle\]

\[= \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi_k^\dagger(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \left( \sum_{i=1}^N \hat{o}_1(r_i) \right) \Psi_l(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\]

\[= \int d\mathbf{r}_1 \hat{o}_1(r_1) \int d\mathbf{s}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi^\dagger(\mathbf{r}_1 s_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \Psi(\mathbf{r}_1 s_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\]

\[+ \cdots + \int d\mathbf{r}_N \hat{o}_1(r_N) \int d\mathbf{x}_1 \cdots d\mathbf{x}_{N-1} d\mathbf{s}_N \Psi^\dagger(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{r}_N s_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{r}_N s_N)\]

\[= \frac{1}{N} \int d\mathbf{r}_1 \rho_{kl}(\mathbf{r}_1) \hat{o}_1(r_1) + \cdots + \frac{1}{N} \int d\mathbf{r}_N \rho_{kl}(\mathbf{r}_N) \hat{o}_1(r_N)\]

\[= \int d\mathbf{r} \rho_{kl}(\mathbf{r}) \hat{o}_1(r) = \int d\mathbf{r} \Omega_{kl}(\mathbf{r}),\] (33)

where the one-electron property density $\Omega_{kl}(\mathbf{r})$ is defined as

\[\Omega_{kl}(\mathbf{r}) := \rho_{kl}(\mathbf{r}) \times \hat{o}_1(r).\] (34)

Therefore a one-electron property can be discussed in the density form.

For the vibronic coupling operators except for constants of the nuclear-nuclear potential derivatives, $\mathbf{O}_1 = \mathbf{W}_a^{(n)} \hat{o}_1 = \hat{w}_a^{(n)}$, and $\Omega_{kl}(\mathbf{r}) = \eta_{a1 \cdots a_n, kl}^{(n)}(\mathbf{r})$. Since the reference geometry $\mathbf{R}_0$ is taken at a stationary point of the reference electronic configuration,

\[\int \rho_0 \times \hat{v}_a(r) d^3 \mathbf{r} + \left( \frac{\partial U_{nn}}{\partial Q_a} \right)_{\mathbf{R}_0} = 0,\] (35)
the first derivative of the nuclear-nuclear potential can be eliminated from the expression of the VCC:

$$V_a = \int \rho_k(r) \times \hat{v}_a(r)d^3r - \int \rho_0(r) \times \hat{v}_a(r)d^3r = \int \Delta \rho_k(r) \times \hat{v}_a(r)d^3r,$$

where $\Delta \rho_k(r)$ is the electron density difference between $\Psi_k$ and the reference state $\Psi_0$. Because of the stationary condition (35), the nuclear-nuclear part of the potential is eliminated from the expression for the linear coupling $V_a$ (36).

For a Slater determinant $\Phi_0$ constructed by orthonormal spin orbitals, $\{ \chi(x_i) = \psi(r_i)\omega(s_i) \}$, a diagonal element of the one-electron property can be decomposed as [14]

$$\langle \Phi_0 | \hat{O}_1 | \Phi_0 \rangle = \sum_{a OCC} n_a \langle \psi_a(r_1) | \hat{o}_1(r_1) | \psi_a(r_1) \rangle,$$

where $n_a$ is the occupation number of $\psi_a$. For an off-diagonal element between $\Phi_0$ and $\Phi^b_a$ with orbital $\psi_a$ in $\Phi_0$ replaced by $\psi_b$,

$$\langle \Phi_0 | \hat{O}_1 | \Phi^b_a \rangle = \langle \psi_a(r) | \hat{o}_1(r) | \psi_b(r) \rangle$$

We define orbital one-electron property density $\omega_{ab}(r)$ as

$$\omega_{ab}(r) := \psi_a^*(r)\psi_b(r)\hat{o}_1(r) = \rho_{ab}(r) \times \hat{o}_1(r),$$

where $\rho_{ab}(r)$ denotes orbital overlap density (transition density). Orbital one-electron property can be decomposed in the density form:

$$\langle \psi_a(r) | \hat{o}_1(r) | \psi_b(r) \rangle = \int \omega_{ab}(r)d^3r.$$  (37)

4. Other Example of One-Electron Property Density: Transition Dipole Moment Density

As an example of the one-electron property, we consider an electric dipole moment operator

$$\hat{\mu} = \sum_i e r_i.$$  (38)

Therefore, $\hat{o}_1 = e r_1$. We define an electric dipole moment density as

$$\tau_{kl}(r) = \rho_{kl}(r) (er).$$  (39)

For an electronic state $\Psi_0$, the diagonal element of $\hat{\mu}$ yields a permanent electric dipole moment of electrons:

$$\mu = \int \rho_0(r)(er)d^3r = \int \tau_{00}(r)d^3r.$$  (40)

The integrand is called a permanent dipole-moment density which is the diagonal element of the electric dipole-moment density.

The off-diagonal element of $\hat{\mu}$ between $\Psi_k$ and $\Psi_l$ is a transition dipole moment.

$$\mu_{kl} = \int \rho_{kl}(r)(er)d^3r = \int \tau_{kl}(r)d^3r,$$

where $\tau_{kl}(r)$ is called the transition dipole moment density (TDMD) which is the off-diagonal element of the electric dipole-moment density. Since absorptions, emissions, and scattering are dominated by the transition dipole moment, we can analyze and control optical processes via the electronic structures of molecules. For example, light-emitting or light-harvesting molecules with high efficiency can be designed based on the TDMD (39). We will investigate the transition dipole moments of anthracene and its derivatives later.
5. Related Concepts to Vibronic Coupling Density

5.1. Orbital Vibronic Coupling Density

Vibronic coupling constant can be decomposed into orbital contributions. The $n$th order orbital vibronic coupling constant (OVCC) between orbitals $\psi_a$ and $\psi_b$ for modes $\alpha_1, \alpha_2, \ldots, \alpha_n$ is defined by

$$\langle \psi_a(\mathbf{r}) | \hat{w}_{\alpha_1 \cdots \alpha_n}(\mathbf{r}) | \psi_b(\mathbf{r}) \rangle. \quad (42)$$

The OVCC is also equal to the spatial integral of a density function $\omega_{\alpha_1 \cdots \alpha_n, ab}(\mathbf{r})$:

$$\langle \psi_a(\mathbf{r}) | \hat{w}_{\alpha_1 \cdots \alpha_n}(\mathbf{r}) | \psi_b(\mathbf{r}) \rangle = \int \rho_{ab}(\mathbf{r}) \times \omega_{\alpha_1 \cdots \alpha_n}(\mathbf{r}) d^3 \mathbf{r} = \int o_{\alpha_1 \cdots \alpha_n, ab}(\mathbf{r}) d^3 \mathbf{r}, \quad (43)$$

where orbital vibronic coupling density (OVCD) is defined as

$$o_{\alpha_1 \cdots \alpha_n, ab}(\mathbf{r}) := \rho_{ab}(\mathbf{r}) \times \omega_{\alpha_1 \cdots \alpha_n}(\mathbf{r}). \quad (44)$$

5.2. Reduced Vibronic Coupling Density

The potential derivatives $\omega_{\alpha_1 \cdots \alpha_n}(\mathbf{r})$ have symmetric distribution near atoms. This gives rise to cancellation as we will see some examples later. We can eliminate such a zero contribution $\eta_{\alpha}^{\prime}(\mathbf{r})$ from $\eta_{\alpha}(\mathbf{r})$ to define the reduced vibronic coupling density (RVCD) $\bar{\eta}_{\alpha}(\mathbf{r})$ which describes net contributions to the VCC [15]:

$$\bar{\eta}_{\alpha}(\mathbf{r}) = \eta_{\alpha}(\mathbf{r}) - \eta_{\alpha}^{\prime}(\mathbf{r}), \quad (45)$$

and

$$\int \eta_{\alpha}^{\prime}(\mathbf{r}) d^3 \mathbf{r} = 0. \quad (46)$$

Therefore,

$$V_{\alpha} = \int \eta_{\alpha}(\mathbf{r}) d^3 \mathbf{r} = \int \bar{\eta}_{\alpha}(\mathbf{r}) d^3 \mathbf{r}. \quad (47)$$

5.3. Atomic Vibronic Coupling Constant

Nuclear-electronic and nuclear-nuclear potentials for nuclei $A$ and $B$ are written as

$$U_{en, A} = \sum_i -\frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|}, \quad (48)$$

and

$$U_{nn, A} = \sum_{B \neq A} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (49)$$

respectively, where $\mathbf{r}_i$ denotes the position of electron $i$, $\mathbf{R}_A$ that of nucleus $A$.

Nuclear-electronic attracting and nuclear-nuclear repulsive potentials are given by

$$U_{en} = \sum_A U_{en, A} = \sum_A \sum_i -\frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|}, \quad (50)$$

and

$$U_{nn} = \frac{1}{2} \sum_A U_{nn, A} = \frac{1}{2} \sum_A \sum_{B \neq A} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (51)$$

respectively.
Atomic vibronic coupling constant (AVCC) is defined as [16]

$$V_{mn,\alpha,A} = \left\langle \Psi_m \left| \left( \frac{\partial U_{en,A}}{\partial Q_\alpha} \right)_{R_0} \right| \Psi_n \right\rangle + \delta_{mn} \left( \frac{\partial U_{nn,A}}{\partial Q_\alpha} \right)_{R_0}. \quad (52)$$

The total sum of the AVCCs over all the nuclei is equal to the VCC:

$$V_\alpha = \sum_A V_{mn,\alpha,A}. \quad (53)$$

Therefore, the AVCC is an atomic contribution to the VCC.

5.4. Effective Vibronic Coupling Density

As we will see later, the VCD for a reaction mode can be regarded as a reactivity index[17]. An effective mode can be a candidate of the reaction mode. The effective mode $s$ is defined by

$$s = \frac{V_\alpha}{\sqrt{\sum_\alpha' V_{\alpha'}^2}} Q_\alpha. \quad (54)$$

The VCD for the effective mode $s$ which is called the effective VCD (EVCD) is defined as

$$\eta_s(r) = \Delta \rho(r) \times \left( \frac{\partial \rho(r)}{\partial s} \right)_{R_0} = \Delta \rho(r) \times v_s(r). \quad (55)$$

6. Applications

In this Section, we present some illustrative examples. All the calculation were performed using the Gaussian09[18].

6.1. Jahn-Teller Couplings in C$_3$H$_3$

The VCD analysis is applied for a Jahn-Teller molecule, C$_3$H$_3$[19]. We have demonstrated a crucial role of orbital relaxation in vibronic couplings based on the VCD analysis. For non-degenerate $\pi$ system, naphthalene anion, the VCCs are overestimated/underestimated without $\sigma$-type polarization taken into consideration[4]. For degenerate $\pi$ system, C$_{60}$ monoanion, the VCD analysis using a broken-symmetry wavefunction also suggests importance of orbital relaxation[10]. Calculations based on a single determinant give rise to a symmetry-broken wavefunction, though the energy splittings of degenerate levels are small in DFT calculations [20]. Nevertheless, for Jahn-Teller systems, a broken-symmetry wavefunction is not appropriate. A computational method in which both symmetry and orbital relaxation can be taken into account is the state-averaged CASSCF method. One should note that for the $\pi$ systems CASSCF calculations including only $\pi$ orbitals in the active space cannot reproduce the $\sigma$-type polarization, and the VCCs will not be reliable in such calculations. Therefore, the active space of the CASSCF calculations must include $\sigma$ as well as $\pi$ orbitals.

We evaluated the VCCs from the state-averaged CASSCF(7,8) wavefunction with the correct symmetry which includes the $\sigma$ orbitals in the active space. The non-degenerate C$_3$H$_3^+$ is considered as the reference system. The optimization and frequency analysis for the reference system were performed within the RHF/STO-3G level of theory. The VCCs were calculated from the analytical gradients in C$_3$H$_3$.

In a single-determinant method, the Hartree-Fock and DFT method, the VCCs of Jahn-Teller modes calculated from wavefunctions with correct symmetries are equal to the OVCCs of the frontier orbitals due to the symmetry of the Clebsh-Gordan coefficients. In the
CASSCF calculation, however, this is not the case, since it includes the orbital relaxations and configuration interactions. For comparison with the VCCs, the OVCCs were estimated from the numerical gradients of the LUMO levels.

Table 1 summarizes the calculated VCCs and OVCCs for the vibronically active modes, $2A_1 \oplus 3E'$, including the reorganization energies calculated from

$$E = \sum_{\alpha} \frac{V_{\alpha}^2}{2\omega_{\alpha}^2}$$  \hspace{1cm} (56)

The symmetric wavefunction yields the VCCs and OVCCs with the correct symmetry of the

| Mode     | $\nu$ (cm$^{-1}$) | $V_\alpha$ | $\Delta \epsilon_L/\Delta Q_\alpha$ |
|----------|-----------------|------------|------------------------------------|
| $A'_1(1)$| 1913.22         | -9.826     | -2.436 -2.436                      |
| $A'_1(2)$| 3757.99         | -13.629    | -14.237 -14.237                    |
| $E'(1)\theta$ | 1059.77     | -2.826     | 3.934 3.938                       |
| $E'(1)\epsilon$ | 1059.77   | -0.003     | 0.051                             |
| $E'(2)\theta$ | 1480.32     | -9.217     | 11.248 11.248                     |
| $E'(2)\epsilon$ | 1480.32    | -0.010     | 0.165                             |
| $E'(3)\theta$ | 3670.56     | -4.603     | 6.430                             |
| $E'(3)\epsilon$ | 3670.56    | -0.005     | 0.082                             |

$E_A$ 259.08 259.08 104.69 104.69
$E_{JT}$ 310.97 310.97 488.23 488.98

Clebsh-Gordan coefficients. Among the Jahn-Teller active modes, $E'(2)$ has the maximum coupling. The OVCCs with respect to $E'$ Jahn-Teller active modes are larger than the corresponding VCCs. This difference between the VCC and the OVCC is explained on the basis of the VCD analysis. The AVCCs are tabulated in Table 2. For the $E'(2)$ mode, the main contribution comes from 1-C.

Table 2. Atomic vibronic coupling constants for C$_3$H$_3$ (10$^{-4}$ a.u.)

| ATOM | $a'_1(1)$ | $a'_1(2)$ | $e'(1)\theta$ | $e'(2)\theta$ | $e'(3)\theta$ | $V_\alpha$ |
|------|-----------|-----------|---------------|---------------|--------------|------------|
| 1-C  | -7.775    | -3.393    | -3.426        | -7.193        | -3.749       | -9.826     |
| 2-C  | -2.741    | -1.196    | 0.467         | -1.304        | 0.535        | -13.629    |
| 3-C  | -2.735    | -1.193    | 0.466         | -1.304        | 0.533        | -2.826     |
| 4-H  | 1.522     | -3.489    | 0.543         | 1.205         | -5.110       | -9.217     |
| 5-H  | 0.951     | -2.180    | -0.439        | -0.310        | 1.595        | -2.436     |
| 6-H  | 0.950     | -2.178    | -0.438        | -0.310        | 1.593        | -2.436     |

Figure 1 shows the LUMO density and the electron density difference. Since the LUMO is a $\pi$ orbital, the positive orbital density $\rho_{\text{LUMO}}(r)$ is distributed outside the molecular plane. On
the other hand, the electron density difference $\Delta \rho$ is different from the orbital density $\rho_{LU}(\mathbf{r})$. It should be noted that the negative contribution which originates from polarizations of doubly occupied $\sigma$ orbitals appears in the molecular plane.

Figure 2 shows the VCD analysis for the $E'(2)$ mode. Since the displacements of the mode and the potential derivative (Figure 2(b)) are in the molecular plane, the $\sigma$ polarization in $\Delta \rho$ yields large contributions in the VCDs. The negative VCD in the molecular plane gives rise to large contribution to the AVCC on 1-C (Figure 2, Table 2). This in-plane VCD originates from the $\sigma$ density and will not appear without the orbital relaxation. The OVCC does not include the $\sigma$-polarization, and hence the OVCCs for the $E'$ modes are larger than the VCCs. Thus, the OVCCs cannot be regarded as the VCCs. The VCD analysis suggests importance of the orbital relaxation in VCC calculations for both the non-Jahn–Teller and Jahn–Teller system.

Figure 1. LUMO density $\rho_{LU}(\theta)$ of C$_3$H$_3$ and $\Delta \rho$ of C$_3$H$_3$. The gray region is positive, and the blue region is negative. Threshold is 0.01 a.u.

Figure 2. (a) Electron density difference $\Delta \rho$, (b) potential derivative $v_{E'(2)}$, and (c) vibronic coupling density $\eta_{E'(2)}$. The isosurface values of (c) is $5 \times 10^{-4}$ a.u.
6.2. Vibronic Couplings and Transition Dipole Moment in the $S_1$ state of Anthracene

Vibronic couplings in the $S_1$ state of anthracene are analyzed in terms of the VCD and transition dipole moments are analyzed in terms of the TDMD in order to enhance the radiative transition and suppress the radiationless transitions.

Diagonal VCCs give rise to vibrational relaxation in excited states. Figure 3 shows the diagonal VCCs in the Franck-Condon $S_1$ state. Mode 53 has the maximum coupling. Figure 4 shows the diagonal VCD analysis for the maximum coupling mode in the Franck-Condon $S_1$ state. The side edge bonds have the large contribution to the VCC. Figure 5 shows the AVCCs for the maximum coupling mode in the Franck-Condon $S_1$ state. The AVCCs on the side edge bonds also indicate the maximum values.

To control the radiationless transitions, we calculated the off-diagonal VCCs between the $S_1$ and $S_0$ states for the adiabatic $S_1$ state. Figure 6 show the off-diagonal VCC between the $S_1$ and $S_0$ states. Figure 7 shows the off-diagonal VCD for the mode 43 between the $S_1$ and $S_0$ states. The large contribution originates from the central carbon atoms.

To enhance radiative transition, we calculated transition dipole moments for anthracene and its derivatives between the $S_1$ and $S_0$ states (Table 3). The TDMD can explain the reason why 9,10-dichloroanthracene has the largest dipole moment. We show the overlap density between the $S_1$ and $S_0$ states of anthracene and its derivatives in Figure 8. The overlap density on the chloride is the origin of the enhancement of transition dipole moment. The TDMDs are shown in Figure 9. The density on the chloride is strengthened because of the product of the $z$ component of the position vector.

Table 3. Transition dipole moments between the $S_1$ and $S_0$ states in $z$ direction $\mu_z$.

|                | $\mu_z$ (a.u.) |
|----------------|----------------|
| Anthracene     | -0.8827        |
| 9-chloroanthracene | -1.1047    |
| 9,10-dichloroanthracene | -1.2322    |
Figure 4. Anthracene in the Franck-Condon $S_1$ ($B_{1u}$) state: (a) maximum-coupling mode $v_{53}$ ($v_{53} = 1683.71$ cm$^{-1}$); (b) derivative of the nuclear-electronic potential with respect to the maximum-coupling mode $v_{53}$ ($|v_{53}| = 1 \times 10^{-2}$ a.u.); (c) electron-density difference $\Delta \rho$ ($|\Delta \rho| = 1 \times 10^{-3}$ a.u.); and (d) vibronic coupling density for the maximum-coupling mode $\eta_{53}$ ($|\eta_{53}| = 1 \times 10^{-5}$ a.u.).

Figure 5. Atomic vibronic coupling constants for the maximum coupling mode of anthracene in the Franck-Condon $S_1$ state. Unit is $1 \times 10^{-5}$ a.u.

The transition dipole moment can be assigned to each atoms. Transition dipole moment between $k$ and $l$ states is express as

$$\mu_{kl} = \langle \Psi_k | \hat{\mu} | \Psi_l \rangle = \sum_\kappa \sum_\lambda D^{kl}_{\kappa \lambda} \langle \phi_\kappa | e \mathbf{r} | \phi_\lambda \rangle,$$  

where $\phi_\kappa$ indicates the basis function $\kappa$ and $D^{mn}_{\kappa \lambda}$ indicates the density matrix. The basis function which belongs to atom $A$ is denoted by $\phi_{\kappa_A}$. Then, an atomic transition dipole moment $\mu^A_{kl}$ can be defined as

$$\mu^A_{kl} = \sum_{\kappa_A} \sum_B \sum_{\lambda_B} D^{kl}_{\kappa_A \lambda_B} \langle \phi_{\kappa_A} | e \mathbf{r} | \phi_{\lambda_B} \rangle.$$  

The sum of the atomic transition dipole moment over all the atoms corresponds to the transition dipole moment. Figure 10 shows the atomic transition dipole moments. The atomic transition dipole moments represent the strength of TDMD in each atom.

The TDMD analyses illustrate that the chlorination enhances the radiative transitions.
Figure 6. Off-diagonal vibronic coupling constants for anthracene between the $S_1$ and $S_0$ states.

Figure 7. Anthracene in the adiabatic $S_1$ state: (a) the second largest coupling mode $\nu_{43}$ ($\nu_{43} = 1354.21 \text{cm}^{-1}$); (b) derivative of the nuclear-electronic potential with respect to the mode 43 $v_{43}$ ($|v_{43}| = 1 \times 10^{-2}$ a.u.); (c) overlap density between the $S_1$ and the $S_0$ states $\rho_{10}$ ($|\rho_{10}| = 5 \times 10^{-3}$ a.u.); and (d) vibronic coupling density for the mode 43 $\eta_{43}$ ($|\eta_{43}| = 5 \times 10^{-5}$ a.u.).
Figure 8. Overlap densities (transition densities) between the S\textsubscript{1} and S\textsubscript{0} states: (a) anthracene, (b) 9-chloroanthracene, and (c) 9,10-dichloroanthracene. Isovalue is $5 \times 10^{-3}$ a.u. White regions are positive; blue regions are negative.

Figure 9. Transition dipole moment densities between the S\textsubscript{1} and S\textsubscript{0} states in z direction: (a) anthracene, (b) 9-chloroanthracene, and (c) 9,10-dichloroanthracene. Isovalue is $1 \times 10^{-2}$ a.u. White regions are positive; blue regions are negative.

Figure 10. Atomic transition dipole moments in z-direction between the S\textsubscript{1} and S\textsubscript{0} states: (a) anthracene, (b) 9-chloroanthracene, and (c) 9,10-dichloroanthracene. Unit is $1 \times 10^{-2}$ a.u.
6.3. Pseudo Jahn-Teller Effect in NH$_3$

The pseudo Jahn–Teller Effect in NH$_3$ [21] is discussed in terms of QVCD and off-diagonal OVCD. Planar NH$_3$ is calculated using the B3LYP/STO-3G level of theory within the $D_3h$ symmetry. The vibrational modes are

$$\Gamma_{\text{vib}} = a'_1 \oplus a''_2 \oplus 2a'. \quad (59)$$

From the vibrational analysis, we obtained an imaginary $a''_2$ mode (902.2724$i$ cm$^{-1}$). For the imaginary $a''_2$ mode, the QVCD and off-diagonal OVCD were calculated. The orbital levels are tabulated in Table 4. Since the HOMO is $a''_2$ and the LUMO is $a'_1$, these levels couple with the

| No. | Irrep. | occupation | orbital energies /a.u. |
|-----|--------|------------|------------------------|
| 1   | $a'_1$ | 2          | -14.048265             |
| 2   | $a'_1$ | 2          | -0.754146              |
| 3   | $e'$   | 2          | -0.406501              |
| 4   | $e'$   | 2          | -0.406501              |
| 5   | $a''_2$| 2          | -0.108744              |
| 6   | $a'_1$ | 0          | 0.350188               |
| 7   | $e'$   | 0          | 0.505624               |
| 8   | $e'$   | 0          | 0.505624               |

$a''_2$ mode:

$$a''_2 \times a'_1 = a''_2. \quad (60)$$

The pseudo Jahn-Teller energy curve for the reference nuclear configuration with the $D_3h$ ($Q_{a''_2} = 0$) is written as

$$E(Q_{a''_2}) \approx E(0) + \frac{1}{2} \left\{ \langle \Psi \left( \partial^2 \hat{H} \left( \frac{\partial \hat{H}}{\partial Q_{a''_2}} \right) \right) \left| \Psi \right\rangle - 2 \frac{\left| \langle \psi_{a''_2} \left| \left( \frac{\partial \hat{H}}{\partial Q_{a''_2}} \right) \right| \psi_{a'_1} \right\rangle^2}{\epsilon_{a'_1} - \epsilon_{a''_2}} \right\} Q_{a''_2}^2,$$

where $\Psi$ denotes the electronic wavefunction, $\psi_{a''_2}$ is the $a''_2$ HOMO, $\psi_{a'_1}$ is the $a'_1$ LUMO, $\epsilon_{a''_2}$ is the orbital level of the HOMO, and $\epsilon_{a'_1}$ is the orbital level of the LUMO.

The QVCD is defined by the integrand of the first term of the right-hand side in

$$\left\langle \psi \left( \partial^2 \hat{H} \right) \left| \psi \right\rangle = \int \rho(r) \times w_{a''_2}(r) d^3r + \left( \frac{\partial^2 U_{nm}}{\partial Q_{a''_2}} \right) \right\rangle, \quad (61)$$

where $w_{a''_2}(r)$ denotes the quadratic potential derivative. The off-diagonal OVCD is the integrand of

$$\left\langle \psi_{a''_2} \left| \left( \frac{\partial \hat{H}}{\partial Q_{a''_2}} \right) \psi_{a'_1} \right\rangle = \int \rho_{\text{HOM}}(r) \times v_{a''_2}(r) d^3r, \quad (62)$$

where $v_{a''_2}(r)$ is the potential derivative. The QVCD is shown in Figure 11. The electron density is totally symmetric, and mainly distributed on the nitrogen atom. However, since the quadratic potential derivative has small distribution on the nitrogen atom, the QVCD is almost equally distributed on the nitrogen and hydrogen atoms.

The OVCD is shown in Figure 13. The OVCD is localized on the nitrogen atoms. This means the pseudo Jahn-Teller instability originates from the lone pair of the nitrogen atoms.
Figure 11. (a) Electron density $\rho(r)$ (isosurface value: $3.0 \times 10^{-1}$ a.u.), (b) imaginary $a''_2$ mode, (c) quadratic potential derivative $w_{a''_2}(r)$ (isovalue: $3.0 \times 10^{-4}$ a.u.), and (d) quadratic vibronic coupling density $\rho(r) \times w_{a''_2}(r)$ (isovalue: $1.0 \times 10^{-4}$ a.u.).

Figure 12. (a) $a''_2$ HOMO (isosurface value: $2.0 \times 10^{-1}$ a.u.), (b) $a'_1$LUMO (isosurface value: $2.0 \times 10^{-1}$ a.u.), and (c) their orbital overlap density $\rho_{HO,LU}(r)$ (isosurface value: $5.0 \times 10^{-3}$ a.u.).

Figure 13. (a) orbital overlap density (transition density) $\rho_{HO,LU}(r)$ (isosurface value: $5.0 \times 10^{-3}$ a.u.), (b) $a''_2$ mode, (c) potential derivative $v_{a''_2}(r)$ (isosurface value: $1.0 \times 10^{-2}$ a.u.), and (d) orbital vibronic coupling density $\rho_{HO,LU}(r) \times v_{a''_2}(r)$ (isosurface value: $1.0 \times 10^{-4}$ a.u.)
6.4. Chemical Reactivity in Nucleophilic Cycloadditions
Regioselectivity for Diels-Alder reactions can be predicted on the basis of the frontier orbital theory [22, 23]. The regioselectivity of the Diels-Alder reaction to C\textsubscript{60} is difficult to be predicted. It has been found that the EVCD is effective to predict the reactivity of C\textsubscript{60}[17]. Here we discuss the regioselectivity in a Diels-Alder reaction to styrene (see Figure 14) using the EVCD. The reactive site of Diels-Alder reaction (b) is the C=\textequiv C bond between \textalpha-C and \textbeta-C. All the calculations were performed at B3LYP/STO-3G level of theory. The LUMO of styrene is delocalized as shown in Figure 15. Figures 16 show the VCD analysis for the effective mode of the styrene anion. The EVCD distribution on \textalpha-C and \textbeta-C is almost the same as that of ethylene as shown in Figure 17. Figure 18 shows the cross section of the EVCD between \textalpha-C and \textbeta-C. Since the EVCD on the bond between \textalpha-C and \textbeta-C is similar to that of ethylene, it is predicted to be the reactive site based on the EVCD analysis.

7. Summary
Linear and nonlinear vibronic couplings are expressed in the density forms. VCDs illustrate the interactions between electronic and vibrational states as local pictures. With help of concepts of OVCD, RVCD, and AVCC, we can analyze and control the vibronic couplings. EVCD can be used as a reactivity index for chemical reactions. Vibronic couplings are one-electron property. We also define TDMD as a one-electron property density. The VCD and TDMD analyses enable

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diels_alder_reactions}
\caption{Diels-Alder reactions.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{lumo_delta_p}
\caption{(a) LUMO (isosurface value: 5.0 \times 10^{-2} \text{ a.u.}) and (b) \Delta\rho(r) (isovalue: 4.0 \times 10^{-3} \text{ a.u.}).}
\end{figure}
Figure 16. Vibronic coupling density analysis for the effective mode of styrene anion. (a) $\Delta \rho(r)$ (isosurface value: $4.0 \times 10^{-3} \text{ a.u.}$), (b) effective mode, (c) $v_s(r)$ (isosurface value: $2.0 \times 10^{-2} \text{ a.u.}$), and (d) $\eta_s(r)$ (isosurface value: $5.0 \times 10^{-5} \text{ a.u.}$).

Figure 17. Comparison of the effective vibronic coupling density for styrene anion to that for ethylene anion. (a) ethylene anion $\eta_e(r)$ (isovalue: $2.0 \times 10^{-4} \text{ a.u.}$) and (b) styrene anion $\eta_s(r)$ (isovalue: $5.0 \times 10^{-5} \text{ a.u.}$).

us to suppress radiationless transitions and enhance radiative transitions with a molecular design. The VCD and TDMD open a way to design light-emitting molecules.

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Figure 18. Effective vibronic coupling density for (a) ethylene anion and (b) styrene anion.

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