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Research paper

Thermodynamical vibronic coupling constant and density: Chemical potential and vibronic coupling in reactions

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ABSTRACT

Vibronic coupling constant (VCC) and density (VCD) defined for a pure state, which have been successfully applied for reactions of fullerenes and nanographenes as reactivity indices, are extended for a mixed state. The extended VCC and VCD, *thermodynamical vibronic coupling constant* (*ThVCC*) and *density* (*ThVCD*), are formulated in the finite-temperature grand-canonical ensemble. ThVCD can be applied for charge transfer of a fractional number of electron. Based on the total differential of chemical potential, the relationship between chemical potential, absolute hardness, and vibronic coupling in a bimolecular reaction is discussed.

1. Introduction

Vibronic coupling density (VCD) [1,2], which is the density form of vibronic (electron–phonon) coupling (VC) [3,4], is a powerful concept that helps us analyze and control vibronic couplings. We have reported molecular designs for carrier-transporting molecules [5,6] and light-emitting molecules [7–9] based on VCD. VCD can also function as a reactivity index [2].

For a bimolecular reaction, donor (D) + acceptor (A) → product (P), a charge-transfer (CT) interaction lowers the activation energy in the initial stage of the reaction as shown in Fig. 1. Frontier orbital theory is based on this lowering of activation energy, which depends on the orientations of D and A [10]. In addition to a CT interaction, the CT state undergoes structural relaxation that originates from VC.

Based on the role of VC in a reaction, VCD has been applied for elucidating the reactivities of Diels–Alder reactions of fullerenes [11–16], metallofullerene [15], and nanographenes [16], whose regioselectivities are difficult to explain based on conventional frontier orbital theory, without considering the effect of VC.

In our previous study, VCD was defined for the electron density $\rho(\mathbf{r})$ of a pure state derived from the wave function $\Psi(\mathbf{R}, \mathbf{r})$ as follows [2]:

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The molecular Hamiltonian $H(\mathbf{R}, \mathbf{r})$ is written as

$$H(\mathbf{R}, \mathbf{r}) = T(\mathbf{R}) + T(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{ne}(\mathbf{R}, \mathbf{r}) + V_{nn}(\mathbf{R}), \tag{1}$$

where

$$T(\mathbf{R}) = -\frac{\hbar^2}{2M_a}\nabla_a^2, \quad T(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla_i^2, \tag{2}$$

$$V_{ee} = \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_j - \mathbf{r}_i|}, \quad V_{nn} = \sum_{a=1}^{M}\sum_{b>a}^{M}\frac{Z_a Z_b e^2}{4\pi\epsilon_0|\mathbf{R}_b - \mathbf{R}_a|}, \tag{3}$$

and

$$V_{ne}(\mathbf{R}, \mathbf{r}) = \sum_{i=1}^{N} v(\mathbf{r}_i), \quad v(\mathbf{r}_i) = \sum_{a=1}^{M} -\frac{Z_a e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{R}_a|}. \tag{4}$$

$\mathbf{R}$ and $\mathbf{r}$ denote a set of nuclear and electronic coordinates, $\mathbf{R}_a$ and $\mathbf{r}_i$, respectively, $T(\mathbf{R})$ and $T(\mathbf{r})$ being the corresponding kinetic energies. m and M_a denote the masses of an electron and a nucleus a, respectively. V_{ee}, V_{nn}, and V_{en} are the potential energies of electron–electron, nucleus–nucleus, and electron–nucleus interactions, respectively. ϵ_0 is the vacuum permittivity, and $v(\mathbf{r}_i)$ denotes the attraction potential of all the nuclei acting on electron i. In the initial stage of the reaction $D + A \rightarrow P$, the charge of the donor D is transferred to the acceptor A. As in the frontier orbital theory, we discuss the regioselectivity of the isolated D/A species. The molecular geometry $\mathbf{R}$ of the CT state of D or A is deformed from the equilibrium geometry $\mathbf{R}_0$ of a reference state by deformation ξ.

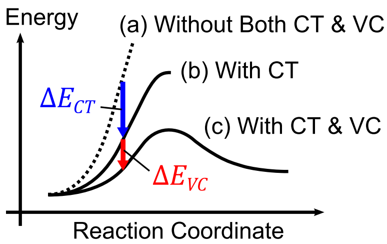

Fig. 1. Reaction profiles. (a) Both CT and VC are ignored. (b) CT is taken into consideration but VC is not. (c) VC as well as CT is considered.

The molecular Hamiltonian of a CT state $\Psi_N(\mathbf{R},\mathbf{r})$ is expanded about the $\mathbf{R}_0$ of a reference state $\Psi_{N_0}(\mathbf{R},\mathbf{r})$ (Hertzberg–Teller expansion):

$$H(\mathbf{R},\mathbf{r}) = H(\mathbf{R}_0,\mathbf{r}) + \left(\frac{\partial H}{\partial \xi}\right)_{\mathbf{R}_0} d\xi + \dots . \tag{5}$$

The direction of deformation ξ, which is written as a sum of the linear combinations of normal vibrational coordinates Q_α for mode α

$$\xi = \sum_{\alpha=1}^{N_{vib}} \zeta_\alpha Q_\alpha, \tag{6}$$

can be regarded as the direction of the reaction path, where N_{vib} denotes the vibrational degrees of freedom,

$$\zeta_\alpha = \frac{V_\alpha}{\sqrt{\sum_{\alpha'} V_{\alpha'}^2}}, \tag{7}$$

and V_α is vibronic coupling constant (VCC) of mode α [1,2] defined later. These active vibrations couple to the electronic states to stabilize the systems, D and A. In the frontier orbital theory, such stabilization due to CT interaction is considered. VC is another origin of the stabilization which is not taken into consideration in the frontier orbital theory.

A VCC can be expressed in terms of VCD. For electron density $\rho_{N_0\pm1}(\mathbf{r})$ derived from the wave function Ψ_N of a system having $N = N_0 \pm 1$ electrons and for that of the reference system having $N = N_0$ electrons, $\rho_{N_0}(\mathbf{r})$, the VCC is written as

$$\begin{aligned} V := &\int \Psi_N^*(\mathbf{R}_0,\mathbf{r}) \left(\frac{\partial H}{\partial \xi}\right)_{\mathbf{R}_0} \Psi_N(\mathbf{R}_0,\mathbf{r}) d\mathbf{r}_1 \dots d\mathbf{r}_i \dots d\mathbf{r}_N \\ &= \int \rho_N(\mathbf{r}_i) w_\xi(\mathbf{r}_i) d\mathbf{r}_i + \left(\frac{\partial V_{nn}}{\partial \xi}\right)_{\mathbf{R}_0} \\ &= \pm \int \Delta\rho(\mathbf{r}_i) w_\xi(\mathbf{r}_i) d\mathbf{r}_i \quad (+ : \text{acceptor}, - : \text{donor}) \\ &= \pm \int \eta_\xi(\mathbf{r}_i) d\mathbf{r}_i \quad (+ : \text{acceptor}, - : \text{donor}), \end{aligned} \tag{8}$$

where the potential derivative $w_\xi(\mathbf{r}_i)$ is defined by

$$w_\xi(\mathbf{r}_i) := \left(\frac{\partial v(\mathbf{r}_i)}{\partial \xi}\right)_{\mathbf{R}_0}, \tag{9}$$

and the electron density difference $\Delta\rho(\mathbf{r}_i)$ is defined as

$$\Delta\rho(\mathbf{r}_i) := \begin{cases} \rho_{N_0+1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r}) & (N = N_0 + 1), \\ \rho_{N_0}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r}) & (N = N_0 - 1). \end{cases} \tag{10}$$

The sign of $\Delta\rho(\mathbf{r}_i)$ for the donor system, $N = N_0 - 1$, is different from that reported in our previous publications. Then, the VCD $\eta_\xi(\mathbf{r}_i)$ is defined by

$$\eta_\xi(\mathbf{r}_i) := \Delta\rho(\mathbf{r}_i) w_\xi(\mathbf{r}_i). \tag{11}$$

Here we employed

$$\int \rho_{N_0}(\mathbf{r}_i) w_\xi(\mathbf{r}_i) d\mathbf{r}_i + \left(\frac{\partial V_{nn}}{\partial \xi}\right)_{\mathbf{R}_0} = 0, \tag{12}$$

since $\mathbf{R}_0$ is the equilibrium geometry for ρ_{N_0}. Hereafter $\mathbf{r}_i$ is simply denoted as $\mathbf{r}$.

The VCD can be employed as a reactivity index, based on the conceptual density functional theory. A ground-state energy functional $E = E[N, v]$ is written as

$$E = E[N, v] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})], \tag{13}$$

where $F[\rho]$ is a universal functional. The total differential of $E = E[N, v]$ is

$$\begin{aligned} dE &= \left(\frac{\partial E}{\partial N}\right)_u dN + \int \left(\frac{\delta E}{\delta v(\mathbf{r})}\right)_N dv(\mathbf{r}) d\mathbf{r} \\ &= \mu dN + \int \rho(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r}, \end{aligned} \tag{14}$$

where $\mu = \mu[N, v]$ is the chemical potential defined by

$$\mu = \mu[N, v] := \left(\frac{\partial E}{\partial N}\right)_v. \tag{15}$$

The total differential of $\mu = \mu[N, v]$ is written as

$$d\mu = \left(\frac{\partial \mu}{\partial N}\right)_v dN + \int \left(\frac{\delta \mu}{\delta v(\mathbf{r})}\right)_N dv(\mathbf{r}) d\mathbf{r} \tag{16}$$

$$= 2\eta dN + \int \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_v dv(\mathbf{r}) d\mathbf{r} \tag{17}$$

$$= 2\eta dN + \int f(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r} \tag{18}$$

$$\approx 2\eta dN + \int \eta_\xi(\mathbf{r}) d\xi d\mathbf{r}, \tag{19}$$

where η is the absolute hardness and $f(\mathbf{r})$ denotes the Fukui function [17], which is approximated as:

$$f(\mathbf{r}) := \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_v \approx \pm(\rho_{N_0\pm1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r})) = \Delta\rho(\mathbf{r}). \tag{20}$$

The VCD for the deformation ξ is defined by

$$\eta_\xi(\mathbf{r}) = \Delta\rho(\mathbf{r}) w_\xi(\mathbf{r}) \approx f(\mathbf{r}) w_\xi(\mathbf{r}). \tag{21}$$

In this letter, we extend the definition of the VCD for the grand-canonical ensemble density functional theory to obtain an exact relation between the chemical potential and vibronic coupling in place of Eq. (19) derived for a pure state in the ground state theory.

2. Theory

2.1. Finite-temperature grand-canonical ensemble density functional theory

Here we summarize the finite-temperature grand-canonical ensemble density functional theory [18].

The grand-canonical ensemble density operator is defined by

$$\hat{\Gamma} := \sum_N \sum_{i_N} p_{Ni_N} |\Psi_{Ni_N}\rangle\langle\Psi_{Ni_N}|, \tag{22}$$

where p_{Ni_N} denotes a statistical weight of an i_Nth pure state having N electrons, $|\Psi_{Ni_N}\rangle$.

The grand-potential functional for equilibrium electron density $\rho(\mathbf{r})$ with chemical potential μ and temperature $\theta = k_BT$ is defined by

$$\Omega[\rho(\mathbf{r})] := F_{GC}[\rho(\mathbf{r})] + \int \rho(\mathbf{r})(v(\mathbf{r}) - \mu) d\mathbf{r}, \tag{23}$$

where $F_{GC}[\rho(\mathbf{r})]$ is the universal functional defined by