VIBRONIC STABILIZATION UNDER THE EXTERNAL APPLIED FIELDS

TAKASHI KATO

Institute for Innovative Science and Technology, Graduate School of Engineering, Nagasaki Institute of Applied Science,
3-1, Shuku-machi, Nagasaki 851-0121, Japan
E-mail: KATO_Takashi@NiAS.ac.jp

Abstract-The relationships between the vibronic and Jahn–Teller stabilization energies, and the Joule's heats, as a function of the external applied electric field, originating from the second- and first-order processes in the vibronic interactions, respectively, are discussed. According to our calculations, a phonon emitted by an electron is received by the same electron, and as a consequence of this nondissipative phonon exchange between two electronic states with opposite momentum and spins, this independent one electron is stabilized in energy. This is the vibronic and Jahn–Teller stabilization energies originating from the second-order processes. On the other hand, in the first-order processes, a phonon emitted dissipatively by an electron is not absorbed by any electron. This is the origin of the electrical resistivity and Joule's heats. The well-known fundamental theorem in physics and chemistry can be naturally explained by our one-electron theory.

Keywords- First-Order Processes; Nondissipative Phonon; Second-First-Order Processes; Vibronic Interactions

I. INTRODUCTION

Vibronic and Jahn–Teller stabilization energies for the opened-shell independent one electron have been calculated and discussed for a long time. However, the mechanism for the occurrence of the vibronic stabilization has not been clear, from the point of view of the second-order processes. In particular, in these discussions, the wavefunction for a moving electron has been ambiguous. And the reason why the vibronic and Jahn–Teller stabilization occur in the opened-shell electronic states in isolated molecular systems in chemistry has not been elucidated, in view of the vibronic interactions via the second-order processes in quantum field theory. Furthermore, the relationships between these energies and the strengths of the external applied electric field have not been discussed in detail. In this article, we discuss how the opened-shell independent one electron is stabilized in energy in view of the second-order processes in the vibronic and electron–phonon interactions in quantum field theory. And, we also discuss the relationships between the vibronic and Jahn–Teller stabilization energies, originating from the nondissipative second-order processes, and the electrical resistivity and Joules's heats, originating from the dissipative first-order processes in the vibronic interactions, as a function of the external applied electric field.

As some examples, we will show that we can naturally explain the well-known fundamental theorem in physics and chemistry by our one-electron theory, as follows. First, we discuss the reason why the most stable electron pairs can be formed by phonon exchanges between two electrons with opposite momentum and spins, as assumed in the conventional two-electrons theory. Next, we also discuss the reason why a metal with higher resistivity at room temperature has larger vibronic stabilization energies at low temperatures, as usually observed. Furthermore, we discuss the reason why spontaneous current states cannot become the most stable in energy without any applied magnetic or electric field, as described in the Bloch's theorem, which has been well known for a long time.

II. THE PROBLEMS IN THE FIRST- AND SECOND-ORDER PROCESSES IN QUANTUM FIELD THEORY IN THE VIBRONIC INTERACTIONS

It has been well known that the first-order processes in phonon-induced scattering of the conduction one electron causes the finite electrical resistivity in the normal metallic or semiconducting states at relatively high temperatures under the external applied magnetic or electric field. On the other hand, such first-order processes are not related to the stabilization energies as a consequence of vibronic interactions and Jahn–Teller effects in the previous researches During the vibronic and Jahn–Teller stabilization processes, the total momentum of electrons should not be changed in any direction and the finite spontaneous currents cannot be expected to occur. This means that a phonon emitted by an electron must be absorbed by an electron in the vibronic and Jahn–Teller stabilization processes. It should be noted that in the second-order processes in vibronic interactions, a phonon emitted from an electron has necessarily to be absorbed by another electron (i.e., nondissipative exchange of phonon), on the other hand, in the first-order processes in vibronic interactions, a phonon emitted from an electron is not

absorbed by another electron (i.e., dissipative emission of phonon). This is the reason why only one electron has been considered to be needed in the first-order processes, on the other hand, two electrons have been considered to be needed in the second-order processes in the vibronic interactions in the conventional theory. Therefore, we have not been able to explain the mechanism how independent opened-shell only one electron can be stabilized in energy as a consequence of the nondissipative phonon exchanges, which need at least two electronic states. That is, we cannot explain the vibronic stabilization energies in the opened-shell one-electron systems in view of the second-order processes in vibronic interactions.

III. STABILIZATION ENERGY AS A CONSEQUENCE OF THE SECOND-ORDER PROCESSES IN QUANTUM FIELD THEORY IN THE VIBRONIC INTERACTIONS IN OUR NEW ONE-ELECTRON MODEL

Let us consider how the second-order processes in vibronic interactions are related to vibronic and Jahn–Teller stabilization energies of independent one electron system under consideration. One electron occupies a plane-wave state , in the absence of interactions, $c_{+\boldsymbol{k}_{\mathrm{LUMO}}}\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle + c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$. The stabilization energy of independent one electron occupying the lowest unoccupied molecular orbitals (LUMO) as a consequence of the vibronic interactions in the second-order processes ($\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$) in a molecule at 0 K can be derived as $\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ $= 2V_{\mathrm{one,LUMO}} f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$, where the $V_{\mathrm{one,LUMO}}$ value denotes the vibronic coupling constant for the interactions between an electron occupying the LUMO and the vibronically active modes, and the $f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ value is closely related to the probability of the occurrence of the second-order processes, and can be expressed as

$$f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right) = 1/2 + c_{-\boldsymbol{k}_{\mathrm{LUMO}}}c_{+\boldsymbol{k}_{\mathrm{LUMO}}} = 1/2 + c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\sqrt{1-c^2_{-\boldsymbol{k}_{\mathrm{LUMO}}}}\,.$$

The $f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ and $\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ values decrease with an increase in the external applied electric field (x_{external}). When no external electric or magnetic field is applied ($x_{\mathrm{external}} = 0$; $\boldsymbol{k}_{\mathrm{total}} = 0$), one electron becomes one of two electronic states at one time, and these two electronic states are rapidly converted evenly ($c^2_{+\boldsymbol{k}_{\mathrm{LUMO}}}(0) = c^2_{-\boldsymbol{k}_{\mathrm{LUMO}}}(0) = 1/2$), and thus the averaged momentum of an independent electron observed for a long time must be zero. This can be also understood from the fact that we cannot expect the spontaneous net charge transfer to any direction without any external applied electric field. Since there are two electronic states with opposite momenta and spins, the second-order processes in vibronic interactions are expected to be applied to these two electronic states $\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ and $\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$. In this case (at $c_{\pm\boldsymbol{k}_{\mathrm{LUMO}}} = 1/\sqrt{2}$), the $\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$ value becomes the maximum value of $2V_{\mathrm{one,LUMO}}$, and one electron is in, the so-called, the vibronic interaction pairing states between two singlet electronic states of $\left|\boldsymbol{k}_{\mathrm{LUMO,one,av.}}\left(1/\sqrt{2},1/\sqrt{2}\right)\right\rangle$ formed by bonding interactions between the $\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ and $\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ states.

The $f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ value decreases with an increase in the external applied electric field, and at $c_{+\boldsymbol{k}_{\mathrm{LUMO}}} = 1$ and $c_{-\boldsymbol{k}_{\mathrm{LUMO}}} = 0$, the $\Delta_{\mathrm{vib,second,one,LUMO}}(1,0)$ value becomes the medium value of $V_{\mathrm{one,LUMO}}$. In such a case, one electron is in, the so-called, the vibronic interaction pairing states between two doublet electronic states $\left|\boldsymbol{k}_{\mathrm{LUMO,one,av.}}(1,0)\right\rangle$ formed by nonbonding interactions between the $\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ and $\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ states. Furthermore, at the very strong external applied electric field ($c_{\pm\boldsymbol{k}_{\mathrm{LUMO}}} = \pm 1/\sqrt{2}$), the $\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},-1/\sqrt{2}\right)$ value becomes the minimum value of 0. In such a case, the electronic states $\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ and $\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ cannot be converted, and one electron is in, the so-called, the vibronic interaction depairing states between two doublet states $\left|\boldsymbol{k}_{\mathrm{LUMO,one,av.}}\left(1/\sqrt{2},-1/\sqrt{2}\right)\right\rangle$ formed by antibonding interactions between the $\left|+\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ and $\left|-\boldsymbol{k}_{\mathrm{LUMO}}\right\rangle$ states.

At $f_{\mathrm{external}}\left(1/\sqrt{2},-1/\sqrt{2}\right) = 0$, the vibronic interaction corresponds to the case where the probability of the occurrence of the second-order processes becomes 0. Usually, very large energy as a consequence of depairing currents are needed in order to destroy the vibronic and Jahn–Teller stabilization states. That is, an electron behaves as if it is occupied in the two electronic states orbitals (

$|+\boldsymbol{k}_{\mathrm{LUMO}}\rangle$ and $|-\boldsymbol{k}_{\mathrm{LUMO}}\rangle$), the characteristics of which change from the bonding interactions to the nonbonding interactions and even to the antibonding interactions with an increase in the external applied electric field.

IV. RELATIONSHIPS BETWEEN OUR NEW ONE-ELECTRON THEORY AND THE CONVENTIONAL TWO-ELECTRONS THEORY IN THE SECOND-ORDER PROCESSES IN VIBRONIC INTERACTIONS

Let us next investigate the relationships between our new one-electron theory and the conventional two-electrons theory in vibronic stabilization processes. Vibronic stabilization energy of bound state two electrons in the two-electrons theory ($\Delta_{\mathrm{vib,second,two,LUMO}}$) without any external applied electric or magnetic field is derived as $V_{\mathrm{two,LUMO}} = 4V_{\mathrm{one,LUMO}}$ $= 2\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$. That is, the only vibronic stabilization energies originating from the vibronic interactions between two electronic states $\left|\boldsymbol{k}_{\mathrm{LUMO,one,av.}}\left(1/\sqrt{2},1/\sqrt{2}\right)\right\rangle$ in our one-electron theory are exactly the same with those in the conventional two-electrons theory, in which no applied external electric field is considered, as expected. Therefore, the assumption that the most stable electron pairs can be formed by phonon exchanges between two electrons with opposite momentum and spins in the conventional two-electrons theory can be well naturally explained by our one-electron theory.

The vibronic interactions between the singlet electronic states are closely related to the second-order processes, and those between the doublet electronic states are closely related to the first-order processes. The second- and first-order processes play less and more important role, respectively, in the vibronic interactions with an increase in the external applied electric field. Furthermore, the relationships between one- and two-electrons theories expressed by $\Delta_{\mathrm{vib,second,two,LUMO}}$) $= 2\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$ are in excellent agreement with the general calculated results derived from the Hückel method. According to our calculated results, two electronic states originating from independent one electron become stabilized because phonon is exchanged between these two electronic states of independent one electron.

That is, phonon emitted by an electron is received by the same electron, and as a consequence of this nondissipative phonon exchange between two electronic states with opposite momentum and spins, this one electron becomes stabilized in energy.

V. RELATIONSHIPS BETWEEN THE VIBRONIC AND JAHN-TELLER STABILIZATION ENERGIES AND THE DISSIPATIVE CURRENT ENERGIES ORIGINATING FROM THE ELECTRICAL RESISTIVITY

Let us next look into the relationships between the vibronic and Jahn–Teller stabilization effects (the second-order processes) and the dissipative current energies originating from the electrical resistivity (mainly, from the first-order processes in vibronic interactions).

Without any external applied electrical field ($x_{\mathrm{external}} = 0$; $f_{\mathrm{external}}\left(1/\sqrt{2},1/\sqrt{2}\right)=1$), the dissipative current energies originating from the electrical resistivity ($\Delta_{\mathrm{resistivity,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$) become zero because there is no current without any external applied electric field ($x_{\mathrm{external}} = 0$; $c_{+\boldsymbol{k}_{\mathrm{LUMO}}} = c_{-\boldsymbol{k}_{\mathrm{LUMO}}}$). In the case of the finite external applied electric field ($f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)\neq 1$ ($c_{+\boldsymbol{k}_{\mathrm{LUMO}}} \neq c_{-\boldsymbol{k}_{\mathrm{LUMO}}}$)), the electronic states are stabilized in energy by the nondissipative phonon exchange second-order processes in the vibronic interactions only by $2V_{\mathrm{one,LUMO}} f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$, because of the extra destabilization energy ($E_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$) originating from the external applied electric field, $\Delta_{\mathrm{vib,total,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ $= \Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ $= 2V_{\mathrm{one,LUMO}} f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$.

On the other hand, at the finite external applied electric field, the finite normal electric currents occur and thus the electronic states can be stabilized in energy by $2V_{\mathrm{one,LUMO}}\left(1-f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)\right)$ as a consequence of the dissipative phonon emission first-order processes in the vibronic interactions (Joule's heats).

Therefore, for very short time, the total stabilization

energy as a consequence of the first-order as well as the second-order processes in the vibronic interactions become $2V_{\mathrm{one,LUMO}}$ even under the external applied electric field,

$$\Delta_{\mathrm{vib,total,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$$
$$=\Delta_{\mathrm{resistivity,one,LUMO}}\left(1/\sqrt{2},-1/\sqrt{2}\right)$$
$$=\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$+\Delta_{\mathrm{vib,first,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=2V_{\mathrm{one,LUMO}}.$$

These stabilization and destabilization processes in the electronic states as a consequence of the first-order processes in the vibronic interactions and the external applied electric field, respectively, are alternately repeated under the external applied electric field.

If the above external applied electric field is switched off ($x_{\mathrm{external}}=0$), the stabilization energy originating from the nondissipative phonon exchange second-order processes in the vibronic interactions can increase from $2V_{\mathrm{one,LUMO}}f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ to $2V_{\mathrm{one,LUMO}}$.

VI. BLOCH'S THEOREM

The $\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ values become the maximum at the equilibrium ground states while the $\Delta_{\mathrm{vib,first,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ values becomes large at the nonequilibrium excited states with finite external electric field, and becomes zero at the equilibrium ground states without any external electric field, and thus the $\Delta_{\mathrm{vib,total,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ ($c_{+\boldsymbol{k}_{\mathrm{LUMO}}}\neq c_{-\boldsymbol{k}_{\mathrm{LUMO}}}$) cannot become the maximum values at the equilibrium ground states as follows,

$$\Delta_{\mathrm{vib,total,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$+\Delta_{\mathrm{vib,first,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=\Delta_{\mathrm{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$<\Delta_{\mathrm{vib,second,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)$$
$$=\Delta_{\mathrm{vib,total,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right).$$

This calculated result derived on the basis of our one-electron theory is in excellent agreement with the well known Bloch's theorem "spontaneous current states ($\Delta_{\mathrm{vib,total,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ ($c_{+\boldsymbol{k}_{\mathrm{LUMO}}}\neq c_{-\boldsymbol{k}_{\mathrm{LUMO}}}$)) cannot become the most stable in energy at the equilibrium ground states without any applied magnetic or electric field ($\Delta_{\mathrm{vib,first,one,LUMO}}\left(1/\sqrt{2},1/\sqrt{2}\right)=0$ ($c_{\pm\boldsymbol{k}_{\mathrm{LUMO}}}=1/\sqrt{2}$))", which has been well known for a long time.

VII. RELATIONSHIPS BETWEEN THE VIBRONIC STABILIZATION ENERGIES AND THE JOULE'S HEATS

At the finite external applied electric field, the finite normal electric currents occur and thus the electronic states can be stabilized in energy by $2V_{\mathrm{one,LUMO}}\left(1-f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)\right)$ as a consequence of the dissipative phonon emission first-order processes in the vibronic interactions. This is the origin of the Joule's heats. The Joule's heats can be defined as

$$\Delta_{\mathrm{resistivity,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=\Delta_{\mathrm{vib,first,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$$
$$=2V_{\mathrm{one,LUMO}}\left(1-f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)\right)$$
$$\propto R_{\mathrm{LUMO}}I^{2}_{\mathrm{LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right),$$

where the R_{LUMO} and $I_{\mathrm{LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ values denote the electrical resistivity and induced currents, respectively.

The R_{LUMO} values are closely related to the $V_{\mathrm{one,LUMO}}$ values, and the $I_{\mathrm{LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ values are closely related to the $\sqrt{1-f_{\mathrm{external}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)}$ values. The $\Delta_{\mathrm{resistivity,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$ value increases with an increase in the external applied electric field. In the normal metallic or semiconducting states, conduction electrons can move according to the applied electric field, and the first-order phonon-induced scattering processes of the conducting electrons ($\Delta_{\mathrm{resistivity,one,LUMO}}\left(c_{+\boldsymbol{k}_{\mathrm{LUMO}}},c_{-\boldsymbol{k}_{\mathrm{LUMO}}}\right)$) become more dominant with an increase in electric field, and causes the finite electrical resistivity at relatively high temperatures.

The second-order phonon-induced stabilization processes of one electron (

$\Delta_{\text{vib,second,one,LUMO}}\left(c_{+\boldsymbol{k}_{\text{LUMO}}}, c_{-\boldsymbol{k}_{\text{LUMO}}}\right)$) become less dominant with an increase in the external applied electric field.

The $\Delta_{\text{resistivity,one,LUMO}}\left(1/\sqrt{2}, -1/\sqrt{2}\right)$ values as well as the $\Delta_{\text{vib,second,one,LUMO}}\left(1/\sqrt{2}, 1/\sqrt{2}\right)$ values increase with an increase in the $V_{\text{one,LUMO}}$ values. Therefore, for example, these results are in excellent agreement with an interesting paradox; a metal with higher resistivity at room temperature has larger vibronic stabilization energies at low temperatures, as usually observed.

VIII. APPLICATION TO THE MACROSCOPIC SIZED CONVENTIONAL SUPERCONDUCTIVITY

Let us next look into the macroscopic sized conventional superconductivity. In our previous researches, we suggested that electron–phonon interactions ($V_{\text{e-ph}}$) play an essential role in the forming of the closed-shell electronic structures with finite valence–conduction band gaps, by which spin singlet electronic states formed by two electrons with opposite momentum and spins ($+\boldsymbol{k}_j\uparrow$ and $-\boldsymbol{k}_j\downarrow$) occupying the same orbitals become stable, and the Coulomb interactions ($E_{\text{Cooper pair}} \approx -V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$) play an essential role in the attractive interactions between these two electrons. Because of the existence of the Coulomb interactions as well as the electron–phonon interactions, electron Cooper pairs can be formed in the macroscopic sized materials, and the conventional superconducting states can appear below T_C, according to our previous researches.

On the other hand, according to the conventional BCS theory, the attractive electron–electron interactions and the energy gaps are formed by the electron–phonon interactions at the same time. We showed in the previous studies that in order to form the energy gaps, two electrons are not needed at the beginning stage of the electron–phonon interactions, which are needed in the conventional BCS theory. That is, we showed that the forming of energy gaps and attractive electron–electron interactions do not necessarily have to occur at the same time. Therefore, the finite energy gaps between the occupied and unoccupied orbitals formed by any origin (for example, by quantization of the orbitals by nature, and by electron–phonon interactions) can be related to the occurrence of superconductivity. That is, both the energy gaps ($\Delta E_{\text{gap}} = \Delta E_{\text{singlet}}$) formed by quantization of the orbitals by nature in the neutral 6an, 10ac, and 14ac, and those formed by electron–phonon interactions in the macroscopic sized superconductivity have equivalent physical meanings, and are closely related to the superconducting transition temperatures ($T_c \propto \Delta E_{\text{gap}}$). In any case, the electron Cooper pairs and supercurrents can be destroyed when the spin singlet states, which are stabilized by the energy gap (ΔE_{gap}) between the occupied and unoccupied orbitals, or the attractive Coulomb interactions ($V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_j\uparrow, -\boldsymbol{k}_j\downarrow\right)$), are destroyed. Therefore, the T_C values can be defined as follows; $T_c = \min\left(\Delta E_{\text{singlet}}, -V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_j\uparrow, -\boldsymbol{k}_j\downarrow\right)\right) = \min\left(\Delta E_{\text{gap}}, -V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_j\uparrow, -\boldsymbol{k}_j\downarrow\right)\right) = \Delta E_{\text{gap}} = \Delta E_{\text{HOMO-LUMO}}$ for the microscopic sized materials, and $= V_{\text{e-ph}}$ for the macroscopic sized materials.

Attractive electron–electron interactions are easily realized, however, the forming of the stable spin singlet states originating from the closed-shell electronic states with small energy gap between the occupied and unoccupied orbitals originating from the electron–phonon interactions is difficult to be realized in the macroscopic sized materials.

That is, the T_C values in superconductivity are related not to the destruction of the attractive Coulomb interactions between two electrons but to the destruction of the spin singlet states formed by the electron–phonon interactions. On the other hand, the spin singlet states originating from the closed-shell electronic states with large energy gap between the occupied and unoccupied orbitals are formed by quantization of orbitals by nature in small sized molecules such as the neutral 6an, 10ac, and 14ac. This is one of the reason why the superconductivity cannot generally be formed, and even if formed, the T_C values are usually very low in the macroscopic sized materials while the nondissipative diamagnetic currents can be usually observed at room temperatures and the T_C values are very large in small sized molecules such as the neutral 6an, 10ac, and 14ac.

Relative relationships between the HOMO–LUMO (valence–conduction band) gaps and the temperatures decide the electronic properties in various materials; room temperatures are very high temperatures for the closed-shell electronic states with small valence–

conduction band gaps in the macroscopic sized superconductors, on the other hand, room temperatures are very low temperatures for the closed-shell electronic states with large HOMO–LUMO gaps in the small sized molecules such as the neutral 6an, 10ac, and 14ac.

The E_{single} and E_{double} values similar to the $\Delta E_{\text{HOMO–LUMO}}(\propto T_{\text{c}})$ values are related to the energies by which the spin singlet states formed by two electrons occupying the HOMO are destroyed. On the other hand, the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair,peak}}$ values are closely related to the direct destruction of strong attractive Coulomb interactions between equivalent two electrons with opposite momentum and spins occupying the HOMO. Our previous theory can be confirmed from the fact that all these photoionizations have been able to be observed. On the other hand, according to the conventional BCS theory, the attractive electron–electron interactions and the energy gaps are formed by the electron–phonon interactions ($V_{\text{e–ph}}$) at the same time.

That is, only electron–phonon interactions ($V_{\text{e–ph}}$) play an essential role in the attractive electron–electron interactions and the forming of the energy gaps. In the BCS theory, the Coulomb interactions are almost completely neglected ($V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)\approx 0$) because the strong electron repulsion between two electrons occupying the HOMO can be reduced by the shielding effects as a consequence of the positive charges of nuclei. That is, according to the conventional BCS theory, the experimental results of the E_{single} and E_{double} values can be observed, but those of the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair,peak}}$ values would not be observed. Therefore, the experimental observations of the $E_{\text{Cooper pair,peak}}$ values of about 70~80 eV cannot be explained by the conventional BCS theory, in which the Coulomb interactions are almost completely neglected, but can be explained by our theory. According to our theory, it can be predicted that the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair,peak}}$ values of about 40~80 eV as well as the E_{double} values of 10^{-1}~10^{-2} eV can be observed in the macroscopic sized conventional superconductivity.

IX. CONCLUDING REMARKS

We discussed the relationships between the vibronic and Jahn–Teller stabilization energies, and the Joule's heats as a consequence of electrical resistivity, originating from the nondissipative second- and dissipative first-order processes in the vibronic interactions, respectively, as a function of the external applied electric field.

The total energies originating from both the second- and first-order processes are constant. According to our calculations, phonon emitted by an electron is received by the same electron, and as a consequence of this phonon exchange between two electronic states with opposite momentum and spins (i.e., nondissipative phonon exchange), this independent one electron is stabilized in energy.

This is the vibronic and Jahn–Teller stabilization energies originating from the second-order processes. On the other hand, in the first-order processes, a phonon emitted by an electron is not absorbed by any electron (i.e., dissipative phonon emission). This is the origin of the electrical resistivity and Joule's heats. The vibronic stabilization energies for the second- and first-order processes decrease and increase, respectively, with an increase in the external applied electric field. We suggest that an electron behaves as if it is occupied in the two electronic states orbitals, the characteristics of which change from the bonding interactions to the nonbonding interactions, and even to antibonding interactions with an increase in the external applied electric field. The assumption that the most stable electron pairs can be formed by phonon exchanges between two electrons with opposite momentum and spins in the conventional two-electrons theory can be well naturally explained by our one-electron theory. And, an interesting paradox "a metal with higher resistivity at room temperature has larger vibronic stabilization energies at low temperatures", can be well rationalized by our one-electron theory. Furthermore, the Bloch's theorem, "spontaneous current states cannot become the most stable in energy without any applied magnetic or electric field", which has been well known for a long time, can be well explained in view of our one-electron theory for the vibronic interactions.

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