

## Complete vibronic Hamiltonian and "hidden" superconductivity

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A field theory of non-Born-Oppenheimer vibronic interaction in a molecular system is formulated using a differential geometrical study of quantum molecular dynamics [A. Tachibana and T. Iwai, *Phys. Rev. A* 33, 2262 (1986)]. In contrast to the conventional approach of many-body formalism, the present approach stresses the finite-system aspects of the theory. The formalism is, of course, general and exact and applies to infinitely large systems. Remarkably, a new vibronically induced interelectron attraction is revealed, which is not brought about by the conventional mechanism of electron-phonon coupling in condensed-matter physics. It is shown that the "sign" of the vibronic interaction with respect to the Coulombic repulsion is  $-$  and is not  $+$  in the conventional electron-phonon coupling model. The physical origin of the newly found interelectron attraction is clarified in terms of the "instantaneous" nature of vibronic interaction and the primordial "spin-flip" mechanism of non-Born-Oppenheimer electron scattering processes [A. Tachibana, K. Hori, and T. Yamabe, *Chem. Phys. Lett.* 112, 279 (1984)]. This predicts a "hidden" vibronic mechanism of superconductivity.

### I. INTRODUCTION

Recently, exotic superconducting states have been found in heavy-fermion superconductors, and the search for a new mechanism of superconductivity is of vital importance.<sup>1</sup> Likewise, a number of conducting organic polymers have been discovered recently and the electric conduction mechanism including electron-phonon coupling which may even lead to superconductivity is one of the fundamental problems in the solid-state properties.<sup>2-5</sup> As conventional BCS theory of superconductivity predicts,<sup>6</sup> the attractive force between a Cooper pair of electrons induced by, e.g., electron-phonon coupling is necessary for superconductivity to occur. In this connection, research on strong-coupling superconductivity<sup>7,8</sup> is a subject of great interest because of the possibility of a high transition temperature. The theory of Little is also well known as a challenge to the prediction of high-temperature superconductivity.<sup>9</sup>

According to electron-phonon coupling in condensed-matter physics, displacements of nuclei from their equilibrium positions should give rise to a perturbing potential acting on electrons.<sup>10</sup> The perturbed electronic state may give rise to a new stable nuclear configuration. In this way, nuclear vibrations and electron-density fluctuations occur synchronously.

The fundamental assumption underlying the conventional treatment of electron-phonon coupling is the existence of a mutually "adiabatic" motion of an electron and nuclear vibration (Born-Oppenheimer approximation). The electron and nuclear vibration are, however, interacting instantaneously and exchanging momenta with each other. In other words, "friction" interaction exists. The interaction is always present for every nuclear configuration. Hence, this may be called an "instantaneous" interaction. Contrary to this, the conventional electron-phonon coupling<sup>10</sup> may be called "delayed." In terms of

the normal coordinate  $Q$  of nuclear vibration, the delayed interaction is caused by small but finite  $Q$ , and the instantaneous interaction is caused by  $\partial/\partial Q$ . The delayed interaction disappears at the equilibrium nuclear configuration, that is, at the origin  $Q=0$ , but the instantaneous interaction exists there. These two kinds of interaction are induced by the same physical origin, that is, nuclear vibration.

Note that these two kinds of interaction should not be confused with each other because they are mutually independent and yet are closely connected with each other. Indeed, the coordinates and momenta are mutually independent dynamical variables and are related to each other through the Poisson bracket in classical mechanics and through the commutator in quantum mechanics. Apparently the new interaction is induced by momentum of nuclear vibration and works instantaneously, and we need no finite displacements of nuclei. The instantaneous interaction has been considered quite small and neglected so far. In other words, the instantaneous interaction has been "hidden" in the history of superconductivity.

In the present paper we shall study quantum mechanics of the newly found instantaneous vibronic interaction which may even lead to superconductivity. Preliminary treatments have been published elsewhere.<sup>11-13</sup> Superconductivity is a highly collective phenomenon, whereas the present theory treats fundamental electronic processes only. We are not in a position, therefore, to consider all aspects of superconductivity at the present stage of the theory. For example, an important point which has to be neglected is the derivation of temperature-dependent phenomenological equations. The considerations of the present paper will then be confined to the *mathematical formulation of the fundamental complete vibronic Hamiltonian*. No approximations or assumptions are adopted to simplify the calculation. The theoretical framework will be presented in Sec. II. Differential geometry is used in

order to define purely vibrational motion in an essentially nonrigid molecular system.<sup>14</sup> The attractive force between a Cooper pair of superconducting electrons will be treated in Sec. III. Since the instantaneous interaction is universal, it exists even in a small molecular system where the finite displacements of nuclear positions do not occur. In this sense, this is a molecular approach to the problem of condensed matter physics. Indeed, this theory can treat polycrystalline or amorphous states where the localized states can play a major role. In Sec. IV virtual absorption and emission of vibrational quanta through the vibronic interaction process is studied. In order to elucidate the present theory, an illustrative example is given in Sec. V. A novel simple rule is described for the attractive force in a one-dimensional polymer. This clearly predicts a hidden superconductivity if the Peierls instability is suppressed, for example, under the condition established by Horovitz and Birnboim.<sup>15</sup> In Sec. VI concluding remarks are given. We treat the nonrelativistic Hamiltonian excluding spin-dependent interactions. Atomic units are used throughout the present paper.

## II. FIELD THEORY OF VIBRONIC INTERACTION

In this section, the complete vibronic interaction is studied in terms of the field-theoretical formalism. A nuclear system of zero total linear and angular momenta is treated, which may be a prerequisite for the molecular system at rest. Translational symmetry of the system is not assumed in this treatment.

### A. Fundamental treatment

For a study of the vibrational motion of a nuclear system in terms of differential geometry,<sup>14</sup> the molecular Hamiltonian is given, under the condition of zero total linear and angular momenta of the nuclear system, by

$$H = \frac{1}{2} \sum_{m,n} J_{\text{int}}^{-1/2} \pi_m J_{\text{int}} a^{mn} \pi_n J_{\text{int}}^{-1/2} + H_e + V_{\text{nucl}}, \quad (2.1a)$$

where the first term is the kinetic energy operator of the vibrational motion of nuclei with

$$\pi_m = J_{\text{int}}^{-1/2} (-i\partial/\partial q^m) J_{\text{int}}^{1/2}, \quad (2.1b)$$

$$J_{\text{int}} = \left[ \left( \frac{\sum_{\alpha} m_{\alpha}}{\prod_{\alpha} m_{\alpha}} \right)^3 \det |I_a \delta_{ab}| / \det |a^{mn}| \right]^{1/2}. \quad (2.1c)$$

In this expression,  $|a^{mn}|$  denotes Wilson's positive definite  $G$  matrix<sup>16</sup> for the internal coordinates  $q^m$  ( $m=1, \dots, 3N_n-6$ ) of the system of  $N_n$  nuclei,  $I_a$  denotes the principal moment of inertia,  $m_{\alpha}$  denotes the mass of the  $\alpha$ th nucleus,  $H_e$  denotes the electronic Hamiltonian, and  $V_{\text{nucl}}$  denotes the potential energy of nuclear repulsions. The momentum operator of vibrational motion is represented by  $\pi_m$ . The  $\pi_m$  satisfy the following commutation relationship:

$$[\pi_m, q^n] = -i\delta_m^n, \quad (2.2a)$$

$$[\pi_m, \pi_n] = 0. \quad (2.2b)$$

If we second quantize the electronic Hamiltonian  $H_e$ , we have

$$H_e = \int a^{\dagger}(1) h(1) a(1) d\tau_1 + \frac{1}{2} \int a^{\dagger}(1) a^{\dagger}(2) (1/r_{12}) a(2) a(1) d\tau_1 d\tau_2, \quad (2.3)$$

where  $a^{\dagger}(1)$  and  $a(1)$  denote the creation and the annihilation operator, respectively, and where  $d\tau_i$  denotes the volume element of the  $i$ th electron including spin variable. Also,  $h(1)$  denotes the one-electron operator and  $1/r_{12}$  denotes the two-electron Coulombic repulsion operator.

The field operators are supposed to be unaffected by nuclear motions because the "bare" electrons and nuclei are mutually independent particles. The independence of the electronic field operators with respect to the nuclear motions may be represented as follows.

First, with respect to the translational motion,

$$[\hat{P}, a(1)] = [\hat{P}, a^{\dagger}(1)] = 0, \quad (2.4a)$$

where  $\hat{P}$  denotes the total linear momentum operator of the nuclear system. Using the center-of-mass coordinate  $X_C$ , we have

$$\hat{P} = -i\partial/\partial X_C. \quad (2.4b)$$

Second, with respect to the rotational motion,

$$[\hat{J}, a(1)] = [\hat{J}, a^{\dagger}(1)] = 0, \quad (2.5a)$$

where  $\hat{J}$  denotes the total angular momentum operator of the nuclear system. Using the Eulerian angles  $\phi^1, \phi^2, \phi^3 = \phi, \theta, \psi$  which specify the orientation of the principal axis frame  $\{e_1, e_2, e_3\}$  with respect to a laboratory frame, we have

$$\hat{J} = \sum_a e_a \hat{J}_a, \quad (2.5b)$$

$$\hat{J}_a = \sum_b R_a^b (-i\partial/\partial \phi^b), \quad (2.5c)$$

where the matrix  $\|R_a^b\|$  is given as<sup>17</sup>

$$\|R_a^b\| = \begin{vmatrix} \text{cosec}\theta \sin\psi & \cos\psi & -\cot\theta \sin\psi \\ \text{cosec}\theta \cos\psi & -\sin\psi & -\cot\theta \cos\psi \\ 0 & 0 & 1 \end{vmatrix}. \quad (2.5d)$$

Third, with respect to the vibrational motion,

$$[\pi_m, a(1)] = [\pi_m, a^{\dagger}(1)] = 0, \quad (2.6)$$

where  $\pi_m$  is given by Eq. (2.1b).

It is to be noted that the nuclear system behaves as an external background system to the electronic Hamiltonian. Hence the molecular orbitals depend on the nuclear configuration parametrically. Let us expand the field operators by the molecular orbitals. Particle-hole representation is adopted,<sup>12</sup>

$$a(1) = \sum_k \psi_k(1) a_k^{\dagger} + \sum_p \psi_p(1) a_p, \quad (2.7)$$

where  $\{k, l\}$  denote the occupied orbitals and  $\{p, q\}$  denote the vacant orbitals of the reference Slater determinant, respectively. We will use  $\{i, j\}$  in order to denote both oc-

cupied and vacant orbitals. Spin variables are implicitly attached to the orbital indices. Here, the reference Slater determinant is represented as

$$|\Phi_0\rangle = \prod_k a_k |0\rangle, \quad (2.8)$$

where  $|0\rangle$  is the vacuum. Since the orbital motion depends on the nuclear configuration parametrically, the nonadiabatic interaction with the nuclear motion appears; Fukutome has called it the recoil effect of electronic orbital motion due to nuclear motion.<sup>18</sup> First, with respect to the translational motion,

$$[\hat{P}, a_k] = -i \left[ \sum_l a_l \langle \psi_l | \partial \psi_k / \partial X_C \rangle + \sum_p a_p^\dagger \langle \psi_p | \partial \psi_k / \partial X_C \rangle \right]. \quad (2.9)$$

Second, with respect to the rotational motion,

$$[\hat{J}, a_k] = -i \sum_a \sum_b e_a R_a^b \left[ \sum_l a_l \langle \psi_l | \partial \psi_k / \partial \phi^b \rangle + \sum_p a_p^\dagger \langle \psi_p | \partial \psi_k / \partial \phi^b \rangle \right]. \quad (2.10)$$

Third, with respect to the vibrational motion,

$$[\pi_m, a_k] = -i \left[ \sum_l a_l \langle \psi_l | \partial \psi_k / \partial q^m \rangle + \sum_p a_p^\dagger \langle \psi_p | \partial \psi_k / \partial q^m \rangle \right]. \quad (2.11)$$

These nonadiabatic interactions exist even if the electrons occupy the vacant orbitals. The interplay between them would be an interesting topic for further investigation of nonadiabaticity.

Since we are studying the vibronic interaction using the Hamiltonian (2.1), we will examine Eq. (2.11) in more detail in Sec. II B.

### B. Dressed vibrational motion

The effect of the vibrational motion on the orbital motion of the electron can be reduced if we introduce a new concept of "dressed" vibrational motion. The physical requirement for such dressed vibrational motion is twofold. If the momentum operator of the dressed vibrational motion is denoted as  $\Pi_m$ , then it should satisfy first the same commutation relationship as the original relationship (2.2),

$$[\Pi_m, q^n] = [\pi_m, q^n], \quad (2.12a)$$

$$[\Pi_m, \Pi_n] = [\pi_m, \pi_n], \quad (2.12b)$$

and second, contrary to Eq. (2.11), the commutability with the field operators of the orbital motion of electron,

$$[\Pi_m, a_i] = [\pi_m, a_i^\dagger] = 0. \quad (2.13)$$

The procedure of construction of such an operator is given as follows.

First, let us introduce the vector coupling operator

$$\kappa_m(1,2) = \frac{1}{2} \sum_i \{ [\pi_m \psi(1)] \psi_i^*(2) + \psi_i(1) [\pi_m \psi_i(2)]^* \}. \quad (2.14a)$$

The Hermiticity of the operator is guaranteed clearly,

$$\kappa_m(1,2) = \kappa_m^*(2,1). \quad (2.14b)$$

The coupling properties are represented as follows:

$$\int \kappa_m(1,2) \psi_i(2) d\tau_2 = -i \partial \psi_i(1) / \partial q^m, \quad (2.14c)$$

$$\int \psi_i^*(1) \kappa_m(1,2) d\tau_1 = i \partial \psi_i^*(2) / \partial q^m, \quad (2.14d)$$

$$\int \kappa_m(1,3) \kappa_n(3,2) d\tau_3 = \sum_i [\partial \psi_i(1) / \partial q^m] (\partial \psi_i^*(2) / \partial q^n). \quad (2.14e)$$

Second, using this vector coupling operator, we define

$$K_m = \int a^\dagger(1) \kappa_m(1,2) a(2) d\tau_1 d\tau_2, \quad (2.15a)$$

satisfying

$$K_m = \sum_k [\pi_m, a_k] a_k^\dagger + \sum_p [\pi_m, a_p^\dagger] a_p, \quad (2.15b)$$

$$[K_m, K_n] = [K_m, \pi_n] + [\pi_m, K_n]. \quad (2.15c)$$

Using these properties, it is easy to prove that the  $K_m$  thus defined satisfy

$$[K_m, a_i] = [\pi_m, a_i], \quad (2.16a)$$

$$[K_m, a_i^\dagger] = [\pi_m, a_i^\dagger]. \quad (2.16b)$$

Then we can construct the dressed vibrational momentum operator as

$$\Pi_m = \pi_m - K_m. \quad (2.17)$$

Clearly, this construction satisfies the criterion given by Eqs. (2.12) and (2.13).

Thus, we have obtained the dressed vibrational momentum operator. The orbital motion of the electron is also dressed instantaneously as will be shown in Sec. II C.

### C. Complete vibronic Hamiltonian

Making use of the dressed vibrational motion in Sec. II B, the vibronic Hamiltonian (2.1a) is rearranged as follows:

$$H = \frac{1}{2} \sum_{m,n} J_{\text{int}}^{-1/2} \Pi_m J_{\text{int}} a^{mn} \Pi_n J_{\text{int}}^{-1/2} + H_{\text{vbr}} + H_e^K + V_{\text{nucl}}, \quad (2.18a)$$

where (i) the first term is the kinetic energy operator of the dressed vibrational motion of nuclei, (ii) the second term, denoted as  $H_{\text{vbr}}$ , is the vibronic or friction interaction operator between the dressed vibrational motion of

nuclei and the dressed electronic motion,

$$E_{\text{vbr}} = \frac{1}{2} \sum_{m,n} J_{\text{int}}^{-1/2} (\Pi_m J_{\text{int}} a^{mn} K_n + K_m J_{\text{int}} a^{mn} \Pi_n) J_{\text{int}}^{-1/2}, \quad (2.18b)$$

$$H_e^K = \frac{1}{2} \sum_k [(F_{kk} + \Delta_{kk}) + h_{kk} + \Delta_{kk}^{(1)}] - \sum_{k,l} (F_{kl} + \Delta_{kl}) a_l^\dagger a_k + \sum_{p,q} (F_{pq} + \Delta_{pq}) a_p^\dagger a_q + \sum_{k,p} [(F_{kp} + \Delta_{kp}) a_k a_p + (F_{pk} + \Delta_{pk}) a_p^\dagger a_k^\dagger] + V_4^K. \quad (2.18c)$$

In this expression, first,  $F_{ij}$  is the matrix element of the well-known Fock operator in terms of the dressed orbital motion of electron,

$$F_{ij} = h_{ij} + \sum_k (\langle ij | kk \rangle - \langle ik | kj \rangle), \quad (2.19a)$$

where the one-electron integral is given as

$$h_{ij} = \langle \psi_i | h | \psi_j \rangle, \quad (2.19b)$$

and the two-electron integral is given as

$$\langle ij | i'j' \rangle = \langle \psi_i(1)\psi_j(2) | 1/r_{12} | \psi_{j'}(2)\psi_{i'}(1) \rangle. \quad (2.19c)$$

Second,  $\Delta_{ij}$  is the matrix element of the nonadiabatic coupling operator represented by

$$\Delta_{ij} = \Delta_{ij}^{(1)} + \Delta_{ij}^{(2)}, \quad (2.20a)$$

and (iii) the third term, denoted as  $H_e^K$ , is the dressed electronic Hamiltonian. The normal product form of  $H_e^K$  is represented as

where the one-electron integral denoted as  $\Delta_{ij}^{(1)}$  is given as

$$\Delta_{ij}^{(1)} = \frac{1}{2} \sum_{m,n} a^{mn} \langle \partial \psi_i / \partial q^m | \partial \psi_j / \partial q^n \rangle, \quad (2.20b)$$

and the two-electron integral denoted as  $\Delta_{ij}^{(2)}$  is given as

$$\Delta_{ij}^{(2)} = \sum_k (\Delta^{(2)} \langle ij | kk \rangle - \Delta^{(2)} \langle ik | kj \rangle), \quad (2.20c)$$

with

$$\Delta^{(2)} \langle ij | i'j' \rangle = - \sum_{m,n} a^{mn} \langle \psi_i | \partial \psi_{j'} / \partial q^m \rangle \langle \partial \psi_j / \partial q^n | \psi_{j'} \rangle. \quad (2.20d)$$

Third, the residual electron correlation term denoted as  $V_4^K$  is given as

$$\begin{aligned} V_4^K = & \frac{1}{2} \sum_{p,q,k,l} (\langle pk | ql \rangle + \Delta^{(2)} \langle pk | ql \rangle) a_p^\dagger a_q^\dagger a_l^\dagger a_k^\dagger - \sum_{p,l,k,l'} (\langle pk | ll' \rangle + \Delta^{(2)} \langle pk | ll' \rangle) a_p^\dagger a_k^\dagger a_l^\dagger a_{l'} \\ & + \sum_{p,q,k,q'} (\langle pk | qq' \rangle + \Delta^{(2)} \langle pk | qq' \rangle) a_k^\dagger a_p^\dagger a_q^\dagger a_{q'} + \frac{1}{2} \sum_{k,l,k',l'} (\langle k'k | l'l \rangle + \Delta^{(2)} \langle k'k | l'l \rangle) a_k^\dagger a_l^\dagger a_{l'} a_{k'} \\ & - \sum_{p,l,k,q} (\langle pq | lk \rangle + \Delta^{(2)} \langle pq | lk \rangle - \langle pk | lq \rangle - \Delta^{(2)} \langle pk | lq \rangle) a_p^\dagger a_k^\dagger a_l a_q \\ & + \frac{1}{2} \sum_{p,q,p',q'} (\langle pp' | qq' \rangle + \Delta^{(2)} \langle pp' | qq' \rangle) a_p^\dagger a_q^\dagger a_{q'} a_{p'} - \sum_{k,l,k',q} (\langle kk' | lq \rangle + \Delta^{(2)} \langle kk' | lq \rangle) a_k^\dagger a_{k'} a_l a_q \\ & - \sum_{p,l,p',q} (\langle pp' | lq \rangle + \Delta^{(2)} \langle pp' | lq \rangle) a_p^\dagger a_{p'} a_q a_l + \frac{1}{2} \sum_{k,l,p,q} (\langle kp | lq \rangle + \Delta^{(2)} \langle kp | lq \rangle) a_k a_l a_q a_p. \end{aligned} \quad (2.21)$$

It should be noted that the orbital motion of the electron is dressed instantaneously and is determined by the dynamic Fock equation given as

$$f_{ij} = \varepsilon_i \delta_{ij}, \quad (2.22a)$$

where

$$f = F + \Delta. \quad (2.22b)$$

The  $\varepsilon_i$  is the energy of the dressed electron orbital. The variational theory of the dynamic Fock equation has also been developed.<sup>11</sup> Using the dressed orbital motion of electron, the dressed electronic Hamiltonian (2.18c) is reduced to

$$H_e^K = E_e^K - \sum_k \varepsilon_k a_k^\dagger a_k + \sum_p \varepsilon_p a_p^\dagger a_p + V_4^K, \quad (2.23a)$$

$$E_e^K = \frac{1}{2} \sum_k (\varepsilon_k + h_{kk} + \Delta_{kk}^{(1)}), \quad (2.23b)$$

where  $V_4^K$  is given in Eq. (2.21). We shall use the dressed electron orbitals in the following development of theory.

The dressed electronic Hamiltonian (2.23) has the character that the orbital motion of electron is dressed by the vibronic interaction. Furthermore the vibronic interaction should alter the nature of the electron correlation significantly. This point is important for interelectron attraction as will be shown in Sec. III.

### III. INSTANTANEOUS INTERELECTRON ATTRACTION

#### A. Spin-flip mechanism

The most important property of the nonadiabatic vibronic interaction is the primordial "spin-flip" mechanism of the electron scattering processes.<sup>12</sup> Indeed, the usual two-electron Coulombic repulsion integral (2.19c) vanishes if the spin functions of the  $ij$  pair (or  $i'j'$  pair) are dif-

ferent from each other. On the other hand, the newly found nonadiabatic two-electron integral (2.20d) vanishes if the spin functions of the  $ij'$  pair (or  $i'j$  pair) are different from each other. This kind of spin-flip mechanism is very characteristic of the vibronic interaction.<sup>12</sup> The spin-flip mechanism plays an important role for the nonadiabatic interelectron attraction as will be shown in Sec. III B.

### B. Interelectron attraction

The novel feature of the newly found nonadiabatic vibronic interaction is most apparent when we consider Cooper pairs of electrons. Before proceeding further, we shall briefly review Anderson's generalization of the Cooper pair.<sup>19</sup> Cooper considered the time-reversal electron pair  $\psi_{k\alpha}$  and  $\psi_{-k\beta}$ , that is, an electron with crystal momentum  $\mathbf{k}$  and up spin, and another electron with op-

posite crystal momentum  $-\mathbf{k}$  and down spin. Anderson generalized this to the time-reversal pair for a dirty superconductor where, because of the loss of translational symmetry, the crystal momentum is no longer a good quantum number.<sup>19,20</sup> The Anderson pair is nothing but a pair of electrons with up spin and down spin and with the same spatial orbital motion. This generalization is quite suitable for discussing the present problem. Indeed, since we treat a large but finite molecular system (or molecular aggregate), however ordered it may be, it is finite and has no translational symmetry globally; thus the crystal momentum is no longer a good quantum number.

It should be noted that  $V_4^x$  given by Eq. (2.21) contains the interaction of Anderson pairs. Then, the spin-flip mechanism described in Sec. III A plays an important role. For example, based on an analogy with particle-hole-type Anderson pairs, we shall prove the vibronic attraction due to the spin-flip mechanism as follows:

$$\begin{aligned} & (\langle p\sigma k\sigma | p\sigma' k\sigma' \rangle + \Delta^{(2)} \langle p\sigma k\sigma | p\sigma' k\sigma' \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger + (\langle p\sigma k\sigma' | p\sigma' k\sigma \rangle + \Delta^{(2)} \langle p\sigma k\sigma' | p\sigma' k\sigma \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger \\ &= \langle p\sigma k\sigma | p\sigma' k\sigma' \rangle a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger + \Delta^{(2)} \langle p\sigma k\sigma' | p\sigma' k\sigma \rangle a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger \\ &= (\langle p\sigma k\sigma | p\sigma' k\sigma' \rangle - \Delta^{(2)} \langle p\sigma k\sigma' | p\sigma' k\sigma \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger. \end{aligned} \quad (3.1)$$

In this and following expressions, the spin variables  $\sigma, \sigma'$  are explicitly shown in addition to the spatial parts of the orbital indices. The key manipulation of the spin-flip mechanism proceeds as follows: (i) from the first line to the second line we use the selection rule of spin variable, and (ii) from the second line to the third line we use the anticommutation relationship.

There are altogether three types of Anderson pairs. The characteristic spin-flip mechanism works equally for these pairs: (i) Anderson pairs of particle-hole type,

$$\frac{1}{2} \sum_{\sigma, \sigma'} \sum_{p, k} (\langle pk | pk \rangle - \Delta^{(2)} \langle pk | pk \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger + \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{k, p} (\langle kp | kp \rangle - \Delta^{(2)} \langle kp | kp \rangle) a_{k\sigma} a_{k\sigma'} a_{p\sigma} a_{p\sigma'}, \quad (3.2)$$

(ii) Anderson pairs of particle-particle type,

$$\frac{1}{2} \sum_{\sigma, \sigma'} \sum_{p, q} (\langle pq | pq \rangle - \Delta^{(2)} \langle pq | pq \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{q\sigma} a_{q\sigma'}, \quad (3.3)$$

and (iii) Anderson pairs of hole-hole type,

$$\frac{1}{2} \sum_{\sigma, \sigma'} \sum_{k, l} (\langle kl | kl \rangle - \Delta^{(2)} \langle kl | kl \rangle) a_{k\sigma} a_{k\sigma'} a_{l\sigma}^\dagger a_{l\sigma'}^\dagger. \quad (3.4)$$

In these and following expressions, the spin variables  $\sigma, \sigma'$  are omitted in the matrix elements for the sake of simplicity. Clearly, the interelectron attraction is guaranteed by the positive definiteness of the vibronic interaction,

$$\begin{aligned} & \Delta^{(2)} \langle ij | ij \rangle \\ &= \sum_{m, n} a^{mn} \langle \psi_i | \partial f / \partial q^m | \psi_j \rangle \\ & \quad \times \langle \psi_i | \partial f / \partial q^n | \psi_j \rangle / (\varepsilon_i - \varepsilon_j)^2 \end{aligned} \quad (3.5a)$$

$$= \sum_n |\langle \psi_i | \partial f / \partial Q_n | \psi_j \rangle|^2 / (\varepsilon_i - \varepsilon_j)^2 \geq 0, \quad (3.5b)$$

where  $Q_n$  denotes the  $n$ th normal vibrational coordinate.

Clearly, we obtain the *selection rule* for a normal mode to participate in the vibronic interaction. If the matrix element of the numerator of Eq. (3.5b) does not vanish

$$\langle \psi_i | \partial f / \partial Q_n | \psi_j \rangle \neq 0, \quad (3.6a)$$

then the  $n$ th normal mode induces the vibronic attraction. Moreover, the orbital energy gap should be infinitely small in order for the vibronic interaction to become significant,

$$|\varepsilon_i - \varepsilon_j| \rightarrow 0. \quad (3.6b)$$

Thus, we have proved the existence of the interelectron attraction induced by the nonadiabatic vibronic interaction. For the special case of a Cooper pair of superconducting electrons, this kind of novel spin-specific interaction has been demonstrated.<sup>12</sup> It should be noted that the interaction is purely instantaneous. In other words, no finite displacements of nuclei are necessary. This dramatic character has not been found in the standard theory of electron-phonon coupling.<sup>10</sup> We summarize this in Table I.

Moreover, it should be noted that as the "size" of the system becomes large, the orbital energy gap  $|\varepsilon_i - \varepsilon_j|$  will become small and then the newly found vibronic interaction will become large. There may exist some critical

TABLE I. Difference of interactions. Conventional electron-phonon coupling in condensed matter physics utilizes delayed interaction between nuclear vibration and electron, while the nonadiabatic vibronic interaction is instantaneous in nature.

Interaction	At equilibrium point $Q=0$
delayed	absent
instantaneous	present

size over which the vibronic interaction becomes so large that it overwhelms the Coulombic repulsion. Then the net attractive force is brought about. This point will be further examined in Sec. IV.

#### IV. MODIFIED INTERELECTRON ATTRACTION

In this section we shall study the effect of virtual electron-vibration scattering processes. This will modify the "exact" vibronic interaction obtained in Sec. III. We shall adopt the local normal coordinate approximation of nuclear vibration. This is valid in the vicinity of the equilibrium configuration of nuclear system.

In order to introduce the equilibrium nuclear configuration, we should provide the potential energy surface. For a preliminary treatment, we shall use the approximate potential energy surface given by the electronic state of the reference Slater determinant.

Let us use the dressed electronic Hamiltonian operator (2.23) on the reference state (2.8). Then we obtain

$$H_e^K |\Phi_0\rangle = E_e^K |\Phi_0\rangle + v_4^K |\Phi_0\rangle, \quad (4.1a)$$

$$v_4^K = \frac{1}{2} \sum_{p,k,q,l} (\langle pk | ql \rangle + \Delta^{(2)} \langle pk | ql \rangle) a_p^\dagger a_q^\dagger a_l^\dagger a_k^\dagger, \quad (4.1b)$$

where  $E_e^K$  is the electronic energy given by Eq. (2.23b), and where  $v_4^K$  is the particle-hole-type interelectron interaction given by the first term of Eq. (2.21). Then, the potential energy surface  $U$  is given by

$$U = E_e^K + V_{\text{nucl}}. \quad (4.2)$$

Using the harmonic approximation of the potential energy surface,

$$U = U_0 + \frac{1}{2} \sum_n \omega_n^2 Q_n^2, \quad (4.3)$$

with the normal coordinate  $Q_n$  and the vibrational frequency  $\omega_n$ , the vibronic Hamiltonian (2.18) is reduced to

$$H = U_0 + \sum_n \omega_n (b_n^\dagger b_n + \frac{1}{2}) + h_{\text{vbr}} + v_4^K, \quad (4.4a)$$

$$h_{\text{vbr}} = \sum_n C_n i \sqrt{\omega_n/2} (b_n^\dagger - b_n), \quad (4.4b)$$

$$C_n = -i \sum_{k,p} \langle \psi_p | \partial \psi_k / \partial Q_n \rangle a_p^\dagger a_k^\dagger, \quad (4.4c)$$

where  $h_{\text{vbr}}$  is the particle-hole-type nonadiabatic interaction energy given by operating  $H_{\text{vbr}}$  of Eq. (2.18b) onto the reference state. In this expression,  $b_n^\dagger$  and  $b_n$  are creation and annihilation operator of the vibrational boson of the  $n$ th normal mode, respectively, satisfying

$$[b_m, b_n^\dagger] = \delta_{mn}. \quad (4.4d)$$

Since we are focusing on Anderson pairs, we shall extract the corresponding portions of operators, denoted by  $A$  in parentheses. For example,  $v_4^K$  contains the interaction of the Anderson pair which will be denoted as  $v_4^K(A)$ ,

$$v_4^K(A) = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{p,k} (\langle pk | pk \rangle - \Delta^{(2)} \langle pk | pk \rangle) a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger; \quad (4.5)$$

correspondingly we obtain  $H(A)$  and  $h_{\text{vbr}}(A)$ .

Using the standard canonical transformation of  $H(A)$ ,

$$\tilde{H}(A) = e^{-S} H(A) e^S, \quad (4.6a)$$

in which only the virtual scattering process with one vibrational quantum (phonon) is involved,<sup>21</sup> the action of  $\tilde{H}(A)$  on the vibrational ground state is reduced to

$$\tilde{H}(A) = U_0 + \frac{1}{2} \sum_n \omega_n + v_4^K(A) + \frac{1}{2} [h_{\text{vbr}}(A), S] + O([h_{\text{vbr}}(A)]^3), \quad (4.6b)$$

where

$$\begin{aligned} \frac{1}{2} [h_{\text{vbr}}(A), S] &= -\frac{1}{2} \sum_n \sum_{\sigma, \sigma'} \sum_{p,k} |\langle \psi_p | \partial f / \partial Q_n | \psi_k \rangle|^2 \\ &\quad \times \omega_n^2 a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger \\ &\quad \times \{(\epsilon_p - \epsilon_k)^2 [(\epsilon_p - \epsilon_k)^2 - \omega_n^2]\}^{-1}. \end{aligned} \quad (4.6c)$$

Neglecting higher-order contributions of  $h_{\text{vbr}}(A)$  in  $\tilde{H}(A)$ , we obtain

$$\begin{aligned} \tilde{H}(A) &= U_0 + \frac{1}{2} \sum_n \omega_n \\ &\quad + \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{p,k} (\langle pk | pk \rangle - \tilde{\Delta}^{(2)} \langle pk | pk \rangle) \\ &\quad \times a_{p\sigma}^\dagger a_{p\sigma'}^\dagger a_{k\sigma}^\dagger a_{k\sigma'}^\dagger, \end{aligned} \quad (4.7a)$$

where  $\tilde{\Delta}^{(2)} \langle pk | pk \rangle$  denotes the modified vibronic interaction,

$$\begin{aligned} \tilde{\Delta}^{(2)} \langle pk | pk \rangle &= \sum_n |\langle \psi_p | \partial f / \partial Q_n | \psi_k \rangle|^2 / [(\epsilon_p - \epsilon_k)^2 - \omega_n^2]. \end{aligned} \quad (4.7b)$$

The exact vibronic interaction given by Eq. (3.5b) has denominator  $(\epsilon_p - \epsilon_k)^2$  in this case, and the modified one given by Eq. (4.7b) has the denominator  $(\epsilon_p - \epsilon_k)^2 - \omega_n^2$ . The modification is then the inclusion of the term  $-\omega_n^2$  in the denominator. It follows that the virtual excitation process may bring about a large attractive interaction if (i) the matrix element of the numerator of the vibronic interaction does not vanish,

$$\langle \psi_p | \partial f / \partial Q_n | \psi_k \rangle \neq 0, \quad (4.8a)$$

and (ii) the infinitesimal limit of the orbital energy gap has the lower bound

$$|\varepsilon_p - \varepsilon_k| \rightarrow \omega_n. \quad (4.8b)$$

The first criterion is the same as Eq. (3.6a), but the second criterion differs from Eq. (3.6b). Since we allow now the exchange of energy with nuclear vibration, the orbital energy difference should have the lower bound. The lower bound is nothing but one quantum of the vibrational (phonon) energy. This new criterion is represented by Eq. (4.8b). These criterions will be examined in Sec. V.

The analog of Eq. (4.7b) is found in the standard textbook approach of electron-phonon coupling.<sup>21,22</sup> But it should be noted that the "sign" of the vibronic interaction with respect to the Coulombic repulsion is  $-$  as shown in Eq. (4.7a) and is not  $+$  as in the well-known attraction model governed by the conventional electron-phonon coupling.<sup>21,22</sup> This is novel to the present instantaneous interaction as compared to the conventional delayed interaction. This may shed new light on the vibronic interaction in the vicinity of the Fermi level, which may even lead to superconductivity. In this sense, this is a hidden vibronic mechanism of superconductivity. The theory will be elucidated in Sec. V using an illustrative analytical model.

## V. EXAMPLE

The theory thus developed is general and therefore is applicable to any type of materials of any size. In this section, we shall examine an illustrative model system in order to elucidate the novel character of the theory. Hence, we shall examine a simple one-dimensional model polymer and reveal the novel asymptotic properties of the modified vibronic interaction  $\tilde{\Delta}^{(2)} \langle pk | pk \rangle$  given by Eq. (4.7b). The lattice points are  $N$  (even) with lattice spacing  $l$  and the number of electrons is  $N$ .

The simple Hückel treatment gives the energy spectra approximately,<sup>13</sup>

$$\varepsilon_i = \alpha + 2\beta \cos[i\pi/(N+1)], \quad i = 1, 2, \dots, N \quad (5.1)$$

$$\omega_n = 2\omega_0 \sin[n\pi/2(N+1)], \quad n = 1, 2, \dots, N. \quad (5.2)$$

In this expression  $\alpha$  is the Coulomb integral,  $\beta$  is the resonance integral, and  $\omega_0$  is the local vibrational frequency. We assume that  $\beta$  is a smooth function of  $l$ ,

$$\beta = \beta(l). \quad (5.3)$$

The wave function of the electron and the vector of vibration are given as follows:

$$c_k^i = [2/(N+1)]^{1/2} \sin(k\rho_i), \quad k = 1, 2, \dots, N \quad (5.4)$$

$$a_k^n = [2/(N+1)]^{1/2} \sin(k\rho_n), \quad k = 1, 2, \dots, N \quad (5.5)$$

where

$$\rho_\lambda = \lambda\pi/(N+1). \quad (5.6)$$

In these expressions  $c_k^i$  denotes the amplitude of the wave function of the  $i$ th electronic state at the  $k$ th site, and  $a_k^n$  denotes the amplitude of the lattice vibration of the  $n$ th

normal vibrational mode at the  $k$ th site, respectively.

The selection rule (4.8a) of the vibronic interaction is represented as

$$p = k + n. \quad (5.7)$$

For finite vibrational quantum number  $n$  the electronic orbital energy levels  $p$  and  $k$  remain in the vicinity of the Fermi level as  $N$  becomes infinitely large. Then the condition (4.8b) is clearly satisfied. Indeed, first, the square of the orbital energy gap becomes infinitely small in inverse proportion to  $N^2$  as  $N \rightarrow \infty$ ,

$$(\varepsilon_p - \varepsilon_k)^2 \rightarrow 4n^2\pi^2\beta^2/N^2. \quad (5.8)$$

Second, by virtue of the selection rule (5.7), the vibrational mode which couples the electron orbitals  $\psi_p$  and  $\psi_k$  is determined uniquely, and the asymptotic behavior of the vibrational energy is given by

$$\omega_n^2 \rightarrow n^2\pi^2\omega_0^2/N^2. \quad (5.9)$$

Third, therefore, one can prove that the condition (4.8b) is clearly satisfied,

$$(\varepsilon_p - \varepsilon_k)^2 - \omega_n^2 \rightarrow 4n^2\pi^2(\beta^2 - \omega_0^2/4)/N^2 > 0, \quad (5.10a)$$

because one can usually assume for mobile electrons the relationship

$$|\beta| \gg \omega_0/2 \quad (5.10b)$$

(this relationship will be examined later). At the same time, the numerator of  $\tilde{\Delta}^{(2)} \langle pk | pk \rangle$  is also positive definite and the asymptotic behavior as  $N \rightarrow \infty$  is given by

$$|\langle \psi_p | \partial f / \partial Q_n | \psi_k \rangle|^2 \rightarrow 8 |\partial\beta/\partial l|^2 / N. \quad (5.11)$$

Note that this diminishes in inverse proportion to  $N$  as  $N \rightarrow \infty$ , and hence will be larger than the denominator given by Eq. (5.10a). It follows that  $\tilde{\Delta}^{(2)} \langle pk | pk \rangle$  tends to infinity in proportion to  $N$  as  $N \rightarrow \infty$ ,

$$\tilde{\Delta}^{(2)} \langle pk | pk \rangle \rightarrow 2N |\partial\beta/\partial l|^2 / n^2\pi^2(\beta^2 - \omega_0^2/4), \quad (5.12)$$

where we used Eqs. (4.7b), (5.7), (5.10), and (5.11). On the other hand, the Coulombic repulsion

$$\langle pk | pk \rangle = \gamma / (N+1), \quad (5.13)$$

where  $\gamma$  denotes the two-electron Coulombic repulsion integral, tends to zero in inverse proportion to  $N$  as  $N \rightarrow \infty$ , independent of  $p$  and  $k$ . Therefore, as  $N \rightarrow \infty$ , the vibronic attraction overwhelms the Coulombic repulsion in the dressed interelectron interaction given by Eq. (4.7a),

$$\langle pk | pk \rangle - \tilde{\Delta}^{(2)} \langle pk | pk \rangle \rightarrow \gamma/N - 2N |\partial\beta/\partial l|^2 / n^2\pi^2(\beta^2 - \omega_0^2/4). \quad (5.14)$$

In other words, there exists a critical number  $N^*$  such that if  $N > N^*$  the dressed interelectron interaction itself becomes attractive,

$$\langle pk | pk \rangle - \tilde{\Delta}^{(2)} \langle pk | pk \rangle < 0 \text{ if } N > N^*. \quad (5.15)$$

This predicts a hidden pairing mechanism which may even lead to superconductivity if the Peierls instability is suppressed, for example, under the condition established

by Horovitz and Birnboim.<sup>15</sup>

It should be noted that, in the strong localization regime, the very reverse of Eq. (5.10b) occurs,

$$|\beta| \ll \omega_0/2, \quad (5.16)$$

and then the vibronic attraction disappears. In this regime superconductivity originating from the vibronic coupling may not be likely to occur. This requires further study, particularly in connection with Anderson localization problems.<sup>23</sup>

Thus, we can estimate (i) the critical size of, and (ii) the degree of "localization" in, the one-dimensional polymer whose vibronically dressed interelectron interaction becomes attractive in the molecular elementary excitation processes.

## VI. CONCLUDING REMARKS

In this paper, the significance of vibronically induced interelectron attraction is demonstrated. The instantaneous nature of the vibronic interaction is emphasized as compared with the conventional delayed electron-phonon coupling model. Since the "spin-flip" mechanism of

non-Born-Oppenheimer scattering processes plays an important role, application of this theory to novel types of superconductivity in heavy-fermion superconductors<sup>1</sup> will be quite interesting, where cooperative action of the vibronic interaction with strong spin-orbit interaction will play an important role. This direction of research is under consideration. Moreover, it should be noted that the formalism of this theory is exact and hence the applicability is universal. This awaits further investigation in future.

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