

## Linking vibrational dynamics to characteristics of local electronic structure: Local analysis of dynamics of the relaxed Si<sub>87</sub> cluster

Lei Liu, C. S. Jayanthi, and Shi-Yu Wu

*Department of Physics, University of Louisville, Louisville, Kentucky 40292, USA*

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A flexible scheme for decomposing the vibrational density of states in terms of the pair vibrational density of states is presented. This scheme provides the linkage between the site vibrational density of states and pair vibrational density of states so that vibrational modes, in particular, localized modes, can be conveniently examined in terms of the correlation between the vibration at a given site and those at its neighboring sites. Furthermore, within the framework of a total-energy vibrational spectrum study, this scheme allows the analysis of vibrational modes in terms of their electronic origin. A case study of the vibrational dynamics of the relaxed Si<sub>87</sub> cluster is carried out to demonstrate the flexibility of the scheme in analyzing the properties of vibrational modes, particularly for complex systems with reduced or no symmetry.

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In recent years, total-energy-vibrational-spectrum studies have been carried out for various systems because of the development of efficient and reliable methods of calculating the total energy.<sup>1-3</sup> These studies start with the calculation of the total energy using semi-empirical tight-binding (TB) approaches<sup>1</sup> or first-principles methods.<sup>2,3</sup> The force-constant matrices between a pair of atoms are then calculated as the appropriate second partial derivatives of the total energy with respect to the displacements of the atoms about their equilibrium positions. While it is indeed more satisfying to calculate the vibrational properties using force-constant matrices determined from the total energy based on quantum-mechanical calculations rather than from an empirically fitted classical potential, a key advantage of the total-energy approaches over the approaches based on the classical potentials is that the former allows the possibility of linking the interesting dynamical features, in particular, vibrational modes associated with surfaces, interfaces, defects, impurities, etc., directly to the local electronic structure. However, this issue has not yet been systematically addressed. We present here a scheme that provides a framework through which dynamic features of a vibrating system can be related to the electronic structure. We also demonstrate the application of this scheme using the vibration dynamics of the relaxed Si<sub>87</sub> cluster as the working example. We show how all the interesting dynamical features of the relaxed Si<sub>87</sub> clusters can be traced to their electronic origins, including the local electronic structure such as bond charges, dangling bonds, etc.

The dynamics of a system is described by the equation of motion

$$\sum_{j\beta} H_{i\alpha,j\beta} c_{j\beta}^\lambda = \omega_\lambda^2 c_{i\alpha}^\lambda, \quad (1)$$

where  $H_{i\alpha,j\beta} = \phi_{i\alpha,j\beta} / \sqrt{m_i m_j}$ ;  $c_{i\alpha}^\lambda = \sqrt{m_i} u_{i\alpha}^\lambda$ , with  $\phi_{i\alpha,j\beta}$  being the force-constant matrix element between atom  $i$  of mass  $m_i$  along the direction  $\alpha$  ( $x, y$ , or  $z$ ) and atom  $j$  of mass  $m_j$  along the direction  $\beta$ , and  $u_{i\alpha}^\lambda$  the eigendisplacement of the  $\lambda$  mode (with the eigen-frequency  $\omega_\lambda$ ) at site  $i$  along the  $\alpha$  direction. Traditionally, the vibrational density of states

(VDOS) projected on sites (individual atoms) is the tool to analyze the nature and properties of a defect or impurity mode. This is usually accomplished by introducing the sum rule  $\sum_{i\alpha} (c_{i\alpha}^\lambda)^2 = 1$  into the defining equation of the VDOS such that  $\rho(\omega) = \sum_\lambda \delta(\omega - \omega_\lambda) = \sum_{\lambda i\alpha} (c_{i\alpha}^\lambda)^2 \delta(\omega - \omega_\lambda)$ . In this way,  $\rho(\omega) = \sum_{i\alpha} \rho_{i\alpha}(\omega)$ , with  $\rho_{i\alpha}(\omega) = \sum_\lambda (c_{i\alpha}^\lambda)^2 \delta(\omega - \omega_\lambda)$  being the local VDOS at site  $i$  along the  $\alpha$  polarization. However, since the force field characterizing a particular vibrational mode is determined by the interaction of the atom at a given site with its neighbors, it is more illuminating if, in addition, the VDOS projected on pairs of atoms is used in combination with the site VDOS to analyze the mode. Thus a sum rule that involves the force-constant matrices would be an appropriate vehicle to construct the VDOS projected onto pairs of atoms. Such a scheme can be set up as follows.

Multiplying the equation of motion with  $c_{i\alpha}^\lambda$  [Eq. (1)], we have<sup>4,5</sup>

$$(c_{i\alpha}^\lambda)^2 = \sum_{j\beta} \frac{H_{i\alpha,j\beta} c_{i\alpha}^\lambda c_{j\beta}^\lambda}{\omega_\lambda^2} = \sum_{j\neq i, \beta} \frac{(u_{i\alpha}^\lambda u_{j\beta}^\lambda - u_{i\alpha}^\lambda u_{i\beta}^\lambda) \phi_{i\alpha,j\beta}}{\omega_\lambda^2}. \quad (2)$$

In arriving at Eq. (2), the relation  $\phi_{i\alpha,i\beta} = -\sum_{j\neq i} \phi_{i\alpha,j\beta}$  has been used. Equation (2) can serve two useful functions. First, the summation of Eq. (2) over both  $i$  and  $\alpha$  leads to

$$\sum_{i\alpha, j\neq i, \beta} \frac{(u_{i\alpha}^\lambda u_{j\beta}^\lambda - u_{i\alpha}^\lambda u_{i\beta}^\lambda) \phi_{i\alpha,j\beta}}{\omega_\lambda^2} = \sum_{i\alpha} (c_{i\alpha}^\lambda)^2 = 1. \quad (3)$$

This is precisely the sum rule needed to project the VDOS onto pairs of atoms  $i$  and  $j$  since Eq. (3) also involves the force-constant matrix elements  $\phi_{i\alpha,j\beta}$ . Thus, when Eq. (3) is inserted into the defining equation for the VDOS, we obtain

$$\begin{aligned} \rho(\omega) &= \sum_{\lambda, i\alpha, j\neq i, \beta} \frac{(u_{i\alpha}^\lambda u_{j\beta}^\lambda - u_{i\alpha}^\lambda u_{i\beta}^\lambda) \phi_{i\alpha,j\beta}}{\omega_\lambda^2} \delta(\omega - \omega_\lambda) \\ &= \sum_{i\alpha, j\neq i, \beta} \rho_{i\alpha,j\beta}(\omega), \end{aligned} \quad (4)$$

where  $\rho_{i\alpha,j\beta}(\omega)$ , the pair VDOS of atom  $i$  along the  $\alpha$  direction and atom  $j$  along the  $\beta$  direction linked by the force-constant matrix element  $\phi_{i\alpha,j\beta}$ , is given by

$$\rho_{i\alpha,j\beta}(\omega) = \sum_{\lambda} \frac{(u_{i\alpha}^{\lambda} u_{j\beta}^{\lambda} - u_{i\alpha}^{\lambda} u_{i\beta}^{\lambda}) \phi_{i\alpha,j\beta}}{\omega_{\lambda}^2} \delta(\omega - \omega_{\lambda}). \quad (5)$$

The second useful function of Eq. (2) is that it provides the framework to link the local VDOS at a particular site to the interactions with its neighbors. In this way, the vibrational mode localized in the vicinity of a given site can be correlated with the vibrational motions of its interacting neighbors. Thus, from Eq. (5), we have

$$\rho_{i\alpha}(\omega) = \sum_{j \neq i, \beta} \rho_{i\alpha,j\beta}(\omega). \quad (6)$$

Equation (2) can also be rewritten as

$$(c_{i\alpha}^{\lambda})^2 = \frac{\sum_{\beta \neq \alpha} \phi_{i\alpha,i\beta} u_{i\alpha}^{\lambda} u_{i\beta}^{\lambda} + \sum_{j \neq i, \beta} \phi_{i\alpha,j\beta} u_{i\alpha}^{\lambda} u_{j\beta}^{\lambda}}{\omega_{\lambda}^2 - H_{i\alpha,i\alpha}}. \quad (7)$$

$\sum_{i\alpha} (c_{i\alpha}^{\lambda})^2 = 1$  then leads to

$$\rho(\omega) = \sum_{i\alpha,j\beta} \bar{\rho}_{i\alpha,j\beta}(\omega) \quad (8)$$

with

$$\begin{aligned} \bar{\rho}_{i\alpha,j\beta}(\omega) &= \sum_{\lambda} \frac{\phi_{i\alpha,j\beta} u_{i\alpha}^{\lambda} u_{j\beta}^{\lambda} - \phi_{i\alpha,i\alpha} (u_{i\alpha}^{\lambda})^2 \delta_{ij} \delta_{\alpha\beta}}{\omega_{\lambda}^2 - H_{i\alpha,i\alpha}} \\ &\times \delta(\omega - \omega_{\lambda}). \end{aligned} \quad (9)$$

Equations (7) and (9) also yield

$$\rho_{i\alpha}(\omega) = \sum_{j\beta} \bar{\rho}_{i\alpha,j\beta}(\omega). \quad (10)$$

Equation (10) allows the decomposition of the site VDOS in terms of on-site as well as off-site contributions.

While the scheme based on Eq. (2) provides the vehicle to decompose the VDOS in terms of contributions from pairs of atoms directly interacting with each other via  $\phi_{i\alpha,j\beta}$ , one may also devise a scheme to project the VDOS onto pairs of atoms interacting directly as well as those not interacting directly. Such a scheme is useful for examining collective (extended) as well as more localized vibrational modes. To develop such a scheme, we note that  $\sum_j c_{j\beta}^{\lambda} = 0$ . This then leads to

$$\sum_{i\alpha,j\beta} c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} = \sum_{i\alpha} (c_{i\alpha}^{\lambda})^2 + \sum_{i\alpha,j\beta} \{c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} - (c_{i\alpha}^{\lambda})^2 \delta_{ij} \delta_{\alpha\beta}\} = 0. \quad (11)$$

Hence,

$$- \sum_{i\alpha,j\beta} \{c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} - (c_{i\alpha}^{\lambda})^2 \delta_{ij} \delta_{\alpha\beta}\} = \sum_{i\alpha} (c_{i\alpha}^{\lambda})^2 = 1. \quad (12)$$

Equation (12) then leads to

$$\rho(\omega) = \sum_{i\alpha,j\beta} \hat{\rho}_{i\alpha,j\beta}(\omega) \quad (13)$$

with

$$\hat{\rho}_{i\alpha,j\beta}(\omega) = - \sum_{\lambda} \{c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} - (c_{i\alpha}^{\lambda})^2 \delta_{ij} \delta_{\alpha\beta}\} \delta(\omega - \omega_{\lambda}). \quad (14)$$

According to Eq. (12), we can also write

$$\rho_{i\alpha}(\omega) = \sum_{j\beta} \hat{\rho}_{i\alpha,j\beta}(\omega). \quad (15)$$

This equation then provides the link of the site VDOS to the pair VDOS  $\hat{\rho}_{i\alpha,j\beta}$ . Similarly  $\sum_j c_{j\beta}^{\lambda} = 0$  leads to

$$\sum_{i\alpha,j} c_{i\alpha}^{\lambda} c_{j\alpha}^{\lambda} = \sum_{i\alpha} (c_{i\alpha}^{\lambda})^2 + \sum_{i\alpha,j \neq i} c_{i\alpha}^{\lambda} c_{j\alpha}^{\lambda} = 0 \quad (16)$$

or

$$\rho(\omega) = \sum_{i\alpha,j \neq i} \tilde{\rho}_{i\alpha,j\alpha}(\omega) \quad (17)$$

with

$$\tilde{\rho}_{i\alpha,j\alpha}(\omega) = - \sum_{\lambda} c_{i\alpha}^{\lambda} c_{j\alpha}^{\lambda} \delta(\omega - \omega_{\lambda}). \quad (18)$$

Equation (16) also leads to

$$\rho_{i\alpha}(\omega) = \sum_j \tilde{\rho}_{i\alpha,j\alpha}(\omega). \quad (19)$$

Equations (2) through (19) provide some examples of projecting the VDOS onto pairs of atom and relating the site VDOS to the pair VDOS for the purpose of studying the correlation between the vibrations at different localities for localized as well as more extended vibrational modes.

Within the framework of a total-energy-vibrational-spectrum approach, the bonding configurations of atoms in the system, such as the bond charges, the nature of the bonds, and the number of bonds associated with each atom, are already determined.<sup>6</sup> Therefore, it is straightforward to relate a particular vibrational mode to its electronic origin via either the site VDOS or the pair VDOS. For example, the VDOS can be partitioned according to the contributions from different ranges of the total bond charge  $q_i = (1/2) \sum_j \sigma_{ij}$  associated with the atom at site  $i$  in the system where  $\sigma_{ij}$  is the bond charge between the pair of atoms  $i$  and  $j$ . This can be accomplished by summing the site VDOS  $\rho_i = \sum_{\alpha} \rho_{i\alpha}$  over those sites  $i$  where  $q_i$  falls within the range  $[a, b]$ , i.e.,

$$\rho(\omega; a \leq q_i \leq b) = \sum_{a \leq q_i \leq b} \rho_i(\omega). \quad (20)$$

Since the bond charge is closely related to the strength of the bond, such a partitioning can shed light on whether a particular mode is associated with the strengthening or weakening of the bonds. Similarly, the VDOS can also be grouped in terms of contributions from atoms possessing a certain number of bonds, namely,

$$\rho(\omega; n_i = k) = \sum_{n_i = k} \rho_i(\omega), \quad (21)$$

where  $n_i$  denotes the number of bonds possessed by the particle  $i$ . This presentation of the vibrational spectrum provides the means to identify the modes associated with dangling bonds and those associated with distorted bonding configurations. To examine how an individual bond affects a particular mode, one may group the pair VDOSs  $\rho_{ij} = \sum_{\alpha\beta} \rho_{i\alpha,j\beta}$  according to the range of the bond charge  $\sigma_{ij}$  such that

$$\rho(\omega; a \leq \sigma_{ij} \leq b) = \sum_{a \leq \sigma_{ij} \leq b} \rho_{ij}(\omega). \quad (22)$$

The characteristics of the bonds are usually described by molecular orbitals such as  $\tau = ss\sigma$ ,  $sp\sigma$ ,  $pp\sigma$ , or  $pp\pi$ . To determine the nature of the bonds responsible for the vibrational modes, one may classify the contribution to a particular mode by a certain bonding type  $\tau$  using

$$\rho(\omega; \tau) = \sum_{i,j \neq i} \left( \sigma_{ij}^\tau / \sum_{\tau} \sigma_{ij}^\tau \right) \rho_{ij}(\omega). \quad (23)$$

The VDOS can also be decomposed in terms of quantities such as the distance, the bond charge, etc. via  $\bar{\rho}_{i\alpha,j\beta}$ ,  $\hat{\rho}_{i\alpha,j\beta}$ , or  $\tilde{\rho}_{i\alpha,j\beta}$ , following a similar procedure as described in Eq. (22). Thus, a very flexible framework that allows the convenient decomposition of the VDOS to pair VDOS via  $\rho_{i\alpha,j\beta}$ , or  $\bar{\rho}_{i\alpha,j\beta}$ , or  $\hat{\rho}_{i\alpha,j\beta}$ , or  $\tilde{\rho}_{i\alpha,j\beta}$ , and the linking of the site VDOS to these pair vibrational density of states [see Eqs. (6), (10), (15), and (19)] can be set up. This framework can then be profitably used to analyze interesting dynamical features of vibrations, in particular, how these features are correlated with the local electronic structure of complex systems with reduced or no symmetry.

To demonstrate the application of the scheme outlined in Eqs. (2) to (23) to examine the properties of the vibrational modes and to trace these modes to their electronic origins, we use the dynamics of a relaxed  $\text{Si}_{87}$  as the working example. The initial configuration of the cluster is an 87-atom tetrahedral network with an atom at the central site. The equilibrium configuration of this cluster was first determined by the molecular-dynamics scheme using the nonorthogonal tight-binding Hamiltonian developed by Mennon and Subbaswamy.<sup>7</sup> The force-constant matrices of the relaxed cluster were then numerically calculated from the total energy.

In Fig. 1, the VDOS of the relaxed cluster, together with contributions to the VDOS from those sites with the total bond charge in a certain range [see Eq. (20)], is shown. We use the bonding configuration of the bulk Si as the reference for choosing the ranges of the total bond charge because Si-based systems favor the tetrahedral  $sp^3$  bonding configuration. In bulk Si, each Si atom contributes  $0.25e$  to one of the four equivalent bonds, giving rise to a total bond charge of  $1e$  for every atom. Thus, we have selected the following four ranges, namely,  $q_i > 1e$ ,  $1e > q_i > 0.8e$ ,  $0.8e > q_i > 0.6e$ , and  $0.6e > q_i$ , to examine the effect of re-

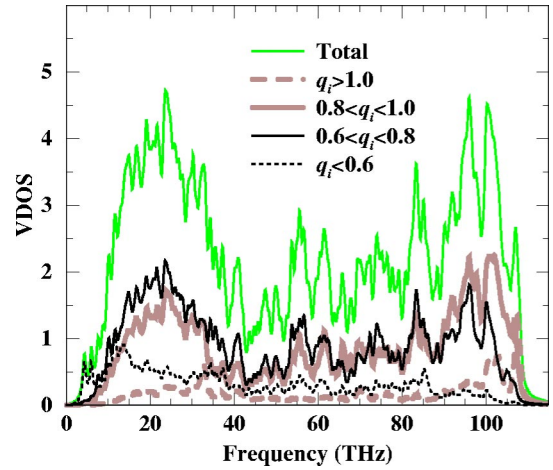


FIG. 1. (Color online) The decomposition of the VDOS in terms of the range of the bond charge  $q_i$  associated with the atoms in the cluster.

laxation on the bonding configuration, and hence on the vibrational spectrum of  $\text{Si}_{87}$ . From Fig. 1, it can be seen that the majority of the contributions to the VDOS originate from those sites with  $1e > q_i > 0.8e$  or  $0.8e > q_i > 0.6e$ , indicating that the relaxation has probably caused a general weakening of the bonds and thus resulting in an overall shift of the VDOS towards lower frequencies compared to the bulk VDOS. Figure 1 also shows that the mode with the highest frequency is a defect mode originating from the range  $q_i > 1e$ , thus a strengthened bonding configuration, while the mode with the lowest frequency originates from the range  $0.6e > q_i$ , a weakened bonding configuration or a configuration with dangling bonds. In Fig. 2, the contribution to the VDOS is decomposed according to the number of bonds associated with each atom [see Eq. (21)]. The existence of a pair of atoms is established by the criterion  $\sigma_{ij} > 0.04e$  rather than relying on the distance.<sup>6</sup> Figure 2 shows that the majority of the contributions still originate from atoms with four bonds, with a significant minority contribution from atoms with three bonds. The defect mode at

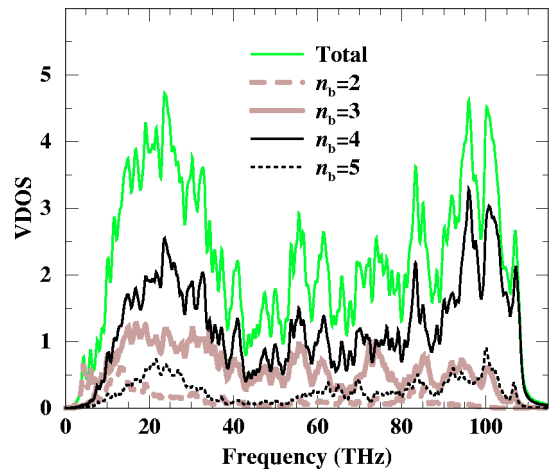


FIG. 2. (Color online) The decomposition of the VDOS in terms of the number of bonds associated with the atoms in the cluster.

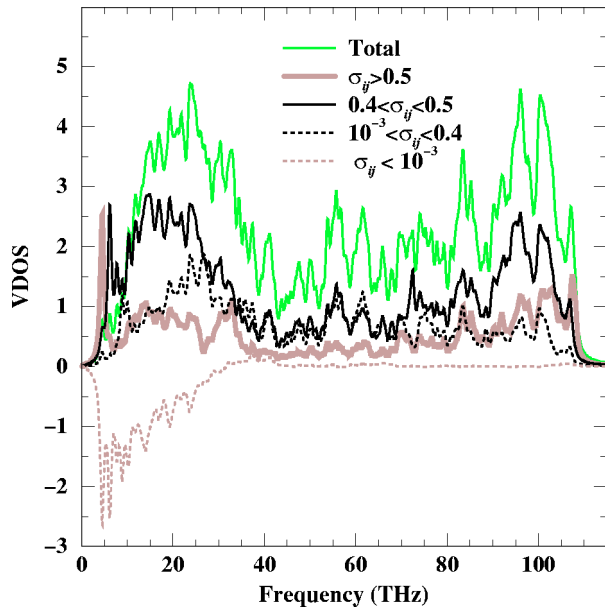


FIG. 3. (Color online) The decomposition of the VDOS in terms of the bond charge  $\sigma_{ij}$  between pairs of atoms in the cluster.

the highest frequency can be seen as associated with an atom with four bonds. Together with the evidence in Fig. 1, it can be concluded that this mode results from the strengthened bonding configuration. The lowest (nonzero) frequency mode, on the other hand, is seen to originate from an atom with two bonds. The evidence provided by Figs. 1 and 2 thus indicates that this mode is a dangling-bond mode, but with remaining bonds strengthened. To further explore this issue, we present in Fig. 3 the decomposition of the VDOS in terms of the ranges of bond charge  $\sigma_{ij}$  [see Eq. (22)]. It can be seen that indeed both the highest- and the lowest-frequency modes are associated with  $\sigma_{ij} > 0.5e$ , indicating that the bonds involved in these vibrations are strengthened bonds (compared to the bulk bond). Figure 3 also shows that the majority of the contributions to the VDOS come from the range  $0.4e < \sigma_{ij} < 0.5e$ , a range with bond charge not too much deviated from the bulk bonding configuration, thus reinforcing the observation provided by Figs. 1 and 2. Another interesting feature in Fig. 3 is the negative contribution in the low-frequency VDOS from the range  $\sigma_{ij} < 10^{-3}e$ . The negative contribution is an indication that for contributions to a certain vibrational mode by pairs of atoms  $i$  and  $j$  interacting via  $\phi_{i\alpha,j\beta}$ , some of those with no chemical bond formed between them may have a force constant too weakened to

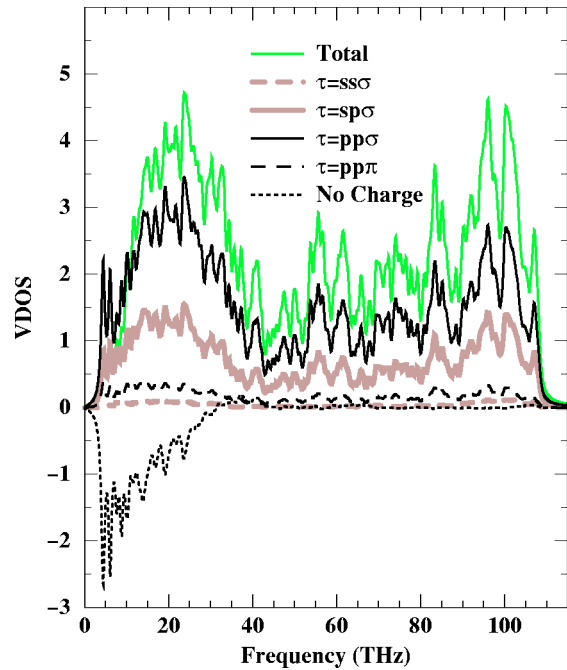


FIG. 4. (Color online) The decomposition of the VDOS according to the bond types.

support the vibration at that frequency. In Fig. 4, we show the decomposition of the VDOS in terms of bonding types [see Eq. (23)]. It can be clearly seen that the main contribution to all the vibrational modes comes from  $pp\sigma$  bonds, with a substantial minority contribution from  $sp\sigma$  bonds. The directional characteristics of the  $pp\sigma$  bonds indicate the dominance of the stretching vibrations, as is expected for a Si-based structure.

The relaxed  $\text{Si}_{87}$  cluster is a system with no symmetry. The demonstration discussed in this paper shows the flexibility of the methodologies developed here to carry out detailed analyses of the dynamics of such a system and to trace interesting dynamical features to their electronic origin. Hence the framework described here is expected to be extremely useful for the study and the analysis of vibrational dynamics of complex systems with low or no symmetry. Effects associated with anharmonicity can also be analyzed using our method by replacing  $H$  in Eq. (1) with an effective dynamical matrix constructed, for example, from a self-consistent quasiharmonic approximation.

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