First-principles theories for anharmonic lattice vibrations

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Size-extensive generalizations of the vibrational self-consistent field (VSCF), vibrational Møller–Plesset perturbation (VMP), and vibrational coupled-cluster (VCC) methods are made to anharmonic lattice vibrations of extended periodic systems on the basis of a quartic force field (QFF) in delocalized normal coordinates. Copious terms in the formalisms of VSCF that have nonphysical size dependence are identified algebraically and eliminated, leading to compact and strictly size-extensive equations. This "quartic" VSCF method (qVSCF) thus defined has no contributions from cubic force constants and alters only the transition energies of the underlying harmonic-oscillator reference from a subset of quartic force constants. It also provides a way to evaluate an anharmonic correction to the lattice structure due to cubic force constants of a certain type. The second-order VMP and VCC methods in the QFF based on the qVSCF reference are shown to account for anharmonic effects due to all cubic and quartic force constants in a size-extensive fashion. These methods can be readily extended to a higher-order truncated Taylor expansion of a potential energy surface in normal coordinates. An algebraic proof of the lack of size-extensivity in the vibrational configuration-interaction method is also presented.
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I. INTRODUCTION

Electronic structures of infinitely extended systems with one-dimensional periodicity (e.g., crystalline polymers) can be characterized accurately by crystalline orbital (CO) theory.[1–3] They are based on size-extensive approximations such as the Hartree–Fock (HF),[4–6] second- and third-order Møller–Plesset perturbations (MP2 and MP3),[7–10] and coupled-cluster singles and doubles methods.[9,10] The corresponding methods for vibrational structures have also been established[11–14] presently for molecules only as the vibrational self-consistent field (VSCF),[15–18] vibrational Møller–Plesset perturbation (VMP),[19–21] vibrational configuration-interaction (VCI),[22] and vibrational coupled-cluster (VCC) methods.[23–26] They allow anharmonicity in potential energy surfaces (PESs) and resulting mode-mode coupling to be accounted for in vibrational spectra[27,28] and vibrationally averaged properties.[29,30] However, these vibrational methods have not thus far been applied to anharmonic lattice vibrations in solids apart from a few notable exceptions[31–33] nor have their formalisms been shown rigorously to have the correct size dependence and be safely applicable to extended systems. For a pioneering analysis of this issue, the reader is referred to Christiansen.[34]

The objective of this study is to present size-extensive generalizations of the VSCF, first- and second-order VMP (VMP1 and VMP2), and VCC methods for extended systems of one-dimensional periodicity in delocalized normal coordinates. The conclusion drawn should be applicable to extended systems of two- and three-dimensional periodicity. The size dependence of the methods is determined by inspecting the asymptotic functional dependence of various quantities that enter their formalisms upon the number (K) of k vectors in the first Brillouin zone (BZ).[3,35] The analysis has revealed that copious terms in the formalisms of VSCF have nonphysical size dependence. These terms have been identified algebraically and eliminated so that compact and strictly size-extensive equations are obtained for a quartic force field (QFF), defining the "quartic" VSCF method (qVSCF) as well as the VMP and VCC methods in a QFF (qVMP and qVCC) based on a qVSCF reference. The qVSCF method has no contributions from cubic force constants and alters only the frequencies of the underlying harmonic-oscillator reference from a subset of quartic force constants. It also provides a way to evaluate an anharmonic correction to the lattice structure due to cubic force constants of a certain type. The VMP2 and VCC methods include the anharmonic effects due to all cubic and quartic force constants in a size-extensive fashion. It is also shown algebraically that VCI lacks size-extensivity. This work reports only the equations defining these methods and a formal analysis of size-extensivity.

II. ELECTRONIC STRUCTURES

This section briefly reviews the established formalism of the MP2 CO method to illustrate the algebraic method of analyzing size-extensivity. In the periodic boundary conditions, a one-dimensional extended system is viewed as a ring

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of K identical repeat units. A symmetry-adapted orbital such as a canonical HF orbital is then delocalized over the entire ring and has the Bloch form

$$\varphi_{pk_p} = K^{-1/2} \sum_{\mu} \sum_{m} c^{\mu}_{pk_p} \exp(-imk_p a) \chi_{\mu}(\mathbf{r} - m\mathbf{a}), \tag{1}$$

where $c^{\mu}_{pk_p}$ is an expansion coefficient, m is the unit cell index and runs over all K unit cells in the system, $\mathbf{a}$ is the lattice vector, and $\chi_{\mu}(\mathbf{r}-m\mathbf{a})$ is the μth atomic orbital (AO) centered in the mth unit cell. Each orbital is characterized by the linear quasimomentum k_p, which can take one of the following K distinct values:

$$k_p = \frac{2n}{K}, \quad \{n \in \mathbb{Z} | 0 \le n < K\}, \tag{2}$$

where the unit of length is adopted in which $|\mathbf{a}| = \pi$. Notice the dual role played by K in the periodic boundary conditions: K is the nominal size of the extended system and also the number of distinct k vectors in the first BZ. We use this knowledge to establish whether a method is size-extensive and therefore applicable to extended systems.[3,35]

Take the MP2 theory[10] as an example. The correlation energy of the entire ring is given by

$$E_{\mathrm{MP2}} = \sum_{i,j,a,b} \sum_{k_i,k_j,k_a} \frac{v^{ik_i jk_j}_{ak_a bk_b} (2v^{ik_i jk_j}_{ak_a bk_b} - v^{ik_i jk_j}_{bk_b ak_a})^*}{e_{ik_i} + e_{jk_j} - e_{ak_a} - e_{bk_b}}, \tag{3}$$

where the CO-based one- and two-electron integrals are related to the AO-based counterparts defined elsewhere[10] by

$$e_{pk_p} = K^0 \sum_{\mu,\nu} \sum_{m} c^{\mu *}_{pk_p} c^{\nu}_{pk_p} \exp(-imk_p a) f^{\mu(0)}_{\nu(m)}, \tag{4}$$

$$v^{pk_p qk_q}_{rk_r sk_s} = K^{-1} \sum_{\kappa,\lambda,\mu,\nu} \sum_{m_1} \sum_{m_2} \sum_{m_3} c^{\kappa *}_{pk_p} c^{\lambda}_{rk_r} c^{\mu *}_{qk_q} c^{\nu}_{sk_s} \times \exp\{i(-m_1 k_r + m_2 k_q - m_3 k_s)a\} v^{\kappa(0)\mu(m_2)}_{\lambda(m_1)\nu(m_3)}. \tag{5}$$

The k summation (BZ integration) in Eq. (3) is only threefold, although there are four distinct k vectors in the summand. This is because the v integrals vanish identically unless the following momentum conservation condition is satisfied:

$$k_i + k_j - k_a - k_b = 2n, \quad \{n \in \mathbb{Z}\}. \tag{6}$$

We can establish[3] the size-extensivity of MP2 by inspecting the K dependence of the quantities entering Eq. (3). The numerator in the equation displays K^{-2} dependence as v is inversely proportional to K [Eq. (5)]. The denominator does not depend on K because of Eq. (4). The threefold k summation gives rise to the factor of K^3. Together they make E_{MP2} exhibit asymptotic K^1 dependence and thus proportional to size, as expected for a size-extensive theory.

III. VIBRATIONAL STRUCTURES

A. Normal coordinates

The normal coordinates and harmonic-oscillator wave functions[36,37] form the basis of our theories. Harmonic force constants of an extended system of one-dimensional periodicity may be obtained in Cartesian coordinates as

$$F_{\mu(0)\nu(m)} = \frac{\partial^2 V}{\partial X_{\mu(0)} \partial X_{\nu(m)}}, \tag{7}$$

where V is an electronic energy of the whole system and $X_{\nu(m)}$ is the νth Cartesian coordinate in the mth unit cell. While V is size-extensive, the force constants are size-intensive because they are associated with spatially local coordinates. Its discrete Fourier transform defines the dynamical force-constant matrix,

$$F^{\mu\nu}_{k} = \sum_{m} F_{\mu(0)\nu(m)} \exp(-imka), \tag{8}$$

and the dynamical mass-weighted force-constant matrix,

$$\tilde{F}^{\mu\nu}_{k} = m^{-1/2}_{\mu} F^{\mu\nu}_{k} m^{-1/2}_{\nu}, \tag{9}$$

where m_{ν} is the atomic mass associated with the νth Cartesian coordinate. The diagonalization of the latter yields squared harmonic frequencies $(\omega^2_{pk_p})$ and normal-mode vectors $(C^{\mu}_{pk_p})$ as eigenvalues and eigenvectors, respectively,

$$\sum_{\nu} \tilde{F}^{\mu\nu}_{k_p} C^{\nu}_{pk_p} = \omega^2_{pk_p} C^{\mu}_{pk_p}. \tag{10}$$

The pth branch of the phonon dispersion curves can be obtained by plotting the frequency ω_{pk_p} as a function of the linear quasimomentum k_p. There are $3N$ such branches (N is the number of atoms in a unit cell), and they are categorized into $3N-4$ $(3N-3)$ optical and 4 (3) acoustic phonon branches (the values in parentheses are for a linelike polymer).

A complex normal coordinate is defined as the orthonormal linear combination of mass-weighted Cartesian coordinates,[38]

$$Q_{pk_p} = K^{-1/2} \sum_{\nu} \sum_{m} m^{1/2}_{\nu} C^{\nu}_{pk_p} \exp(-imk_p a) X_{\nu(m)}, \tag{11}$$

which satisfies $Q^*_{pk_p} = Q_{p-k_p}$. In the BO approximation, the vibrational Hamiltonian is

$$\hat{H}_{\mathrm{n}} = -\frac{1}{2} \sum_{p} \sum_{k_p} \frac{\partial^2}{\partial Q^*_{pk_p} \partial Q_{pk_p}} + V, \tag{12}$$

where V (the potential energy surface or PES) is an electronic energy of the whole system (not an energy per unit cell). In the harmonic approximation,

$$V = V_{\mathrm{HRM}} \equiv \frac{1}{2} \sum_{p} \sum_{k_p} \omega^2_{pk_p} Q^*_{pk_p} Q_{pk_p}. \tag{13}$$

The normal coordinates of the first kind,[38] which are real, can be defined by

$$Q_{pk_p} = 2^{-1/2}(q_{pk_p} + i\bar{q}_{pk_p}), \tag{14}$$

$$Q^*_{pk_p} = 2^{-1/2}(q_{pk_p} - i\bar{q}_{pk_p}), \tag{15}$$

except when $k_p=0$ in which case $Q_{p0}=Q^*_{p0}=q_{p0}$ ($\bar{q}_{p0}$ is not defined). They satisfy the relations, $q_{p-k_p}=q_{pk_p}$ and $\bar{q}_{p-k_p}=-\bar{q}_{pk_p}$, and therefore, the nonredundant set of independent k vectors in these coordinates spans just one half BZ. In these coordinates, the Hamiltonian in the harmonic approximation reduces to the sum of the Hamiltonians of independent harmonic oscillators,

$$\hat{H}_{\mathrm{HRM}} = -\frac{1}{2}\sum_p {\sum_{k_p}}' \frac{\partial^2}{\partial q^2_{pk_p}} - \frac{1}{2}\sum_p {\sum_{k_p}}' \frac{\partial^2}{\partial \bar{q}^2_{pk_p}} + \frac{1}{2}\sum_p {\sum_{k_p}}' \omega^2_{pk_p} q^2_{pk_p} + \frac{1}{2}\sum_p {\sum_{k_p}}' \omega^2_{pk_p} \bar{q}^2_{pk_p}, \tag{16}$$

where the primes indicate that the summations are taken over only the nonredundant set of k vectors. The vibrational Schrödinger equation of this Hamiltonian is subject to complete separation of variables and can thus be solved exactly. For a state characterized by a string of quantum numbers $\mathbf{v} \equiv v_{1k_0}\ldots v_{(3N)k_{K/2}}\bar{v}_{1k_1}\ldots\bar{v}_{(3N)k_{K/2}}$, the wave function and energy of the whole system are given by

$$\Phi^{\mathbf{v}}_{\mathrm{HRM}} = \prod_p {\prod_{k_p}}' \eta^{v_{pk_p}}_{pk_p}(q_{pk_p}) \prod_p {\prod_{k_p}}' \eta^{\bar{v}_{pk_p}}_{pk_p}(\bar{q}_{pk_p}), \tag{17}$$

$$E^{\mathbf{v}}_{\mathrm{HRM}} = \sum_p {\sum_{k_p}}' \omega_{pk_p}(v_{pk_p} + 1/2) + \sum_p {\sum_{k_p}}' \omega_{pk_p}(\bar{v}_{pk_p} + 1/2), \tag{18}$$

where the symbols with overbars are associated with $\bar{q}_{pk_p}$ and those without overbars with q_{pk_p}. The one-mode wave function with the quantum number v_{pk_p} is

$$\eta^{v_{pk_p}}_{pk_p}(q_{pk_p}) = N_{v_{pk_p}} H_{v_{pk_p}}(\omega^{1/2}_{pk_p} q_{pk_p}) \exp(-\omega_{pk_p} q^2_{pk_p}/2). \tag{19}$$

The explicit expressions of the normalization coefficients $N_{v_{pk_p}}$ and the Hermite polynomials $H_{v_{pk_p}}$ are found in many places.[39] The functional forms of $\eta^{v_{pk_p}}_{pk_p}$ and $\eta^{\bar{v}_{pk_p}}_{pk_p}$ are identical to each other when $v_{pk_p}=\bar{v}_{pk_p}$. It is evident that ω_{pk_p} and $E^{\mathbf{v}}_{\mathrm{HRM}}$ are K^0 (size-intensive) and K^1 (size-extensive) quantities, respectively.

B. Anharmonic potential energy functions

There are a number of ways to approximate V.[40] In view of the enormous dynamical degrees of freedom in an extended system, one practical way will be to expand V in a Taylor series and truncate it after a finite order. A QFF (Refs. 41 and 42) in the normal coordinates is written as

$$V = \sum_p F_{p0}Q_{p0} + \frac{1}{2!}\sum_{p,q}\sum_{k_p} F_{pk_pqk_q}Q_{pk_p}Q_{qk_q} + \frac{1}{3!}\sum_{p,q,r}\sum_{k_p,k_q} F_{pk_pqk_qrk_r}Q_{pk_p}Q_{qk_q}Q_{rk_r} + \frac{1}{4!}\sum_{p,q,r,s}\sum_{k_p,k_q,k_r} F_{pk_pqk_qrk_rsk_s}Q_{pk_p}Q_{qk_q}Q_{rk_r}Q_{sk_s} \tag{20}$$

$$= \sum_p F_{p0}q_{p0} + \frac{1}{2!2}\sum_{p,q}\sum_{k_p} F_{pk_pqk_q}(q_{pk_p}q_{qk_q} + 2iq_{pk_p}\bar{q}_{qk_q} - \bar{q}_{pk_p}\bar{q}_{qk_q}) + \frac{1}{3!2^{3/2}}\sum_{p,q,r}\sum_{k_p,k_q} F_{pk_pqk_qrk_r}(q_{pk_p}q_{qk_q}q_{rk_r} + 3iq_{pk_p}q_{qk_q}\bar{q}_{rk_r} - 3q_{pk_p}\bar{q}_{qk_q}\bar{q}_{rk_r} - i\bar{q}_{pk_p}\bar{q}_{qk_q}\bar{q}_{rk_r}) + \frac{1}{4!2^2}\sum_{p,q,r,s}\sum_{k_p,k_q,k_r} F_{pk_pqk_qrk_rsk_s}(q_{pk_p}q_{qk_q}q_{rk_r}q_{sk_s} + 4iq_{pk_p}q_{qk_q}q_{rk_r}\bar{q}_{sk_s} - 6q_{pk_p}q_{qk_q}\bar{q}_{rk_r}\bar{q}_{sk_s} - 4iq_{pk_p}\bar{q}_{qk_q}\bar{q}_{rk_r}\bar{q}_{sk_s} + \bar{q}_{pk_p}\bar{q}_{qk_q}\bar{q}_{rk_r}\bar{q}_{sk_s}), \tag{21}$$

where the summations take into consideration the fact that the force constants (F) in the normal coordinates vanish identically unless the sum of the momenta is conserved (see below). The second equality follows from Eqs. (14) and (15). When the k summations are taken over the whole first BZ (as in the above equation), the factor of $2^{-1/2}$ needs to be associated with each q_{pk_p} or $\bar{q}_{pk_p}$ except q_{p0}. This exception is not made explicit for notational simplicity unless k vectors are specifically zero.

The following analysis does not substantially depend on this particular truncation order and can thus be extended readily to a higher-order truncated Taylor expansion of V (if not to a grid-based numerical representation). As will become clear, cubic and quartic force constants give rise to leading-order anharmonic contributions to lattice structures and energies, respectively, and, in this sense, a QFF is the lowest-order truncation that is meaningful for the analysis.

In the Cartesian coordinates, the same QFF can be expressed as

$$V = \sum_{\kappa}\sum_{m_1} F_{\kappa(m_1)}X_{\kappa(m_1)} + \frac{1}{2!}\sum_{\kappa,\lambda}\sum_{m_1,m_2} F_{\kappa(m_1)\lambda(m_2)}X_{\kappa(m_1)}X_{\lambda(m_2)} + \frac{1}{3!}\sum_{\kappa,\lambda,\mu}\sum_{m_1,m_2,m_3} F_{\kappa(m_1)\lambda(m_2)\mu(m_3)}X_{\kappa(m_1)}X_{\lambda(m_2)}X_{\mu(m_3)} + \frac{1}{4!}\sum_{\kappa,\lambda,\mu,\nu}\sum_{m_1,m_2,m_3,m_4} F_{\kappa(m_1)\lambda(m_2)\mu(m_3)\nu(m_4)}X_{\kappa(m_1)}X_{\lambda(m_2)}X_{\mu(m_3)}X_{\nu(m_4)} \quad (22)$$

$$= K\sum_{\kappa} F_{\kappa(0)}X_{\kappa(0)} + \frac{K}{2!}\sum_{\kappa,\lambda}\sum_{m_1} F_{\kappa(0)\lambda(m_1)}X_{\kappa(0)}X_{\lambda(m_1)} + \frac{K}{3!}\sum_{\kappa,\lambda,\mu}\sum_{m_1,m_2} F_{\kappa(0)\lambda(m_1)\mu(m_2)}X_{\kappa(0)}X_{\lambda(m_1)}X_{\mu(m_2)} + \frac{K}{4!}\sum_{\kappa,\lambda,\mu,\nu}\sum_{m_1,m_2,m_3} F_{\kappa(0)\lambda(m_1)\mu(m_2)\nu(m_3)}X_{\kappa(0)}X_{\lambda(m_1)}X_{\mu(m_2)}X_{\nu(m_3)}, \quad (23)$$

where the second equality exploits the translational invariance of the force constants in the Cartesian coordinates such as

$$F_{\kappa(m_1)\lambda(m_2)\mu(m_3)\nu(m_4)} = F_{\kappa(0)\lambda(m_2-m_1)\mu(m_3-m_1)\nu(m_4-m_1)}. \quad (24)$$

The factor of K that multiplies each sum in Eq. (23) underscores the fact that the terms in V are individually size-extensive (K^1). The two sets of force constants are related to each other by the following transformations:

$$F_{pk_p} = K^{1/2}\Delta_{k_p}\sum_{\kappa} m_{\kappa}^{-1/2}C_{pk_p}^{\kappa *}F_{\kappa(0)}, \quad (25)$$

$$F_{pk_pqk_q} = K^0\Delta_{k_p+k_q}\sum_{\kappa,\lambda}\sum_{m_1} m_{\kappa}^{-1/2}m_{\lambda}^{-1/2}C_{pk_p}^{\kappa *}C_{qk_q}^{\lambda *}F_{\kappa(0)\lambda(m_1)} \times \exp(im_1k_qa), \quad (26)$$

$$F_{pk_pqk_qrk_r} = K^{-1/2}\Delta_{k_p+k_q+k_r}\sum_{\kappa,\lambda,\mu}\sum_{m_1,m_2} m_{\kappa}^{-1/2}m_{\lambda}^{-1/2}m_{\mu}^{-1/2} \times C_{pk_p}^{\kappa *}C_{qk_q}^{\lambda *}C_{rk_r}^{\mu *}F_{\kappa(0)\lambda(m_1)\mu(m_2)} \times \exp\{i(m_1k_q + m_2k_r)a\}, \quad (27)$$

$$F_{pk_pqk_qrk_rsk_s} = K^{-1}\Delta_{k_p+k_q+k_r+k_s}\sum_{\kappa,\lambda,\mu,\nu}\sum_{m_1,m_2,m_3} m_{\kappa}^{-1/2}m_{\lambda}^{-1/2}m_{\mu}^{-1/2} \times m_{\nu}^{-1/2}C_{pk_p}^{\kappa *}C_{qk_q}^{\lambda *}C_{rk_r}^{\mu *}C_{sk_s}^{\nu *}F_{\kappa(0)\lambda(m_1)\mu(m_2)\nu(m_3)} \times \exp\{i(m_1k_q + m_2k_r + m_3k_s)a\}, \quad (28)$$

where Δ ensures that these force constants are nonvanishing when and only when the normal coordinates involved satisfy the momentum conservation condition,[38] namely,

$$\Delta_k = K^{-1}\sum_{m}\exp(ikma) = \begin{cases} 1 & k = 2n \ \{n \in \mathbb{Z}\} \\ 0 & \text{otherwise}. \end{cases} \quad (29)$$

These expressions indicate that the nth-order force constants in the normal coordinates scale as $K^{1-n/2}$ (Ref. 38). Furthermore, since the normal coordinates are centered at the equilibrium lattice structure, we have

$$F_{pk_p} = 0, \quad (30)$$

$$F_{pk_pqk_q} = \delta_{pq}\Delta_{k_p+k_q}\omega_{pk_p}^2. \quad (31)$$

C. Self-consistent field theory

A VSCF wave function[15–17] of the state characterized by the string of quantum numbers $\mathbf{v}$ is the product,

$$\Phi_{\mathrm{VSCF}}^{\mathbf{v}} = \prod_p \prod_{k_p}{}' \zeta_{pk_p}^{v_{pk_p}}(q_{pk_p})\prod_p \prod_{k_p}{}' \zeta_{pk_p}^{\bar{v}_{pk_p}}(\bar{q}_{pk_p}), \quad (32)$$

where $\zeta_{pk_p}^{v_{pk_p}}$ is a one-mode function (modal) of q_{pk_p} with the quantum number v_{pk_p} and the linear quasimomentum k_p in the pth phonon branch and $\zeta_{pk_p}^{\bar{v}_{pk_p}}$ defined accordingly. It is expanded as a linear combination of the harmonic-oscillator wave functions with the same p and k_p attributes,

$$\zeta_{pk_p}^{v}(q_{pk_p}) = \sum_{w} D_{pk_p}^{wv}\eta_{pk_p}^{w}(q_{pk_p}), \quad (33)$$

where D is an expansion coefficient and some subscripts are omitted for notational simplicity. We vary ζ such that the expectation value of $\hat{H}_{\mathrm{n}}$ in the wave function $\Phi_{\mathrm{VSCF}}^{\mathbf{v}}$ becomes a minimum. This leads to coupled eigenvalue equations that need to be solved self-consistently for all p's and k_p's,

$$\sum_{w} G_{pk_p}^{uw}D_{pk_p}^{wv} = D_{pk_p}^{uv}E_{pk_p}^{v}, \quad (34)$$

where $E_{pk_p}^{v}$ is the energy of the modal $\zeta_{pk_p}^{v}$ and $G_{pk_p}^{uw}$ is an element of the matrix representation of $\hat{G}$ in the harmonic-oscillator basis,

$$G_{pk_p}^{uw} = \langle \eta_{pk_p}^{u}|\hat{G}_{pk_p}^{\mathbf{v}}|\eta_{pk_p}^{w}\rangle, \quad (35)$$

with

$$\hat{G}_{pk_p}^{\mathbf{v}} = -\frac{1}{2}\frac{\partial^2}{\partial q_{pk_p}^2} + U_{pk_p}^{\mathbf{v}}(q_{pk_p}). \quad (36)$$

Here U is an effective one-mode (thus one-dimensional) potential for the mode pk_p and is the expectation value of V in the product of all modals except for the one in question,

$$U_{pk_p}^{\mathbf{v}}(q_{pk_p}) = \langle \Phi_{pk_p}^{\mathbf{v}}|V|\Phi_{pk_p}^{\mathbf{v}}\rangle, \quad (37)$$

with

$$\Phi_{pk_p}^{\mathbf{v}} = \Phi_{\mathrm{VSCF}}^{\mathbf{v}}/\zeta_{pk_p}^{v_{pk_p}}(q_{pk_p}). \quad (38)$$

Through this potential, Eq. (34) for one mode couples with the corresponding equations for all the other modes.

When V is a QFF, U is also a quartic function of q_{pk_p} and is written as

$$U^{v}_{pk_p}(q_{pk_p}) = U_0 + U_1 q_{pk_p} + \frac{1}{2!}U_2 q^2_{pk_p} + \frac{1}{3!}U_3 q^3_{pk_p} + \frac{1}{4!}U_4 q^4_{pk_p}. \tag{39}$$

Let us first clarify what the correct dependence of U should be. Note that U is a one-dimensional potential for the mode pk_p, whose associated kinetic energy part scales as K^0. The third and subsequent terms that depend on q_{pk_p} must therefore scale as K^0 and determine the size-intensive (K^0) transition energies and the shapes of the modals. The first term (U_0), on the other hand, is a constant representing the sum of the energies of all the other modes and should be size-extensive (K^1). The second term ($U_1 q_{pk_p}$) should be zero for U to have the correct size dependence. We shall now show, however, that Eq. (39) does not formally satisfy these criteria.

Substituting Eq. (21) into Eq. (37), we find the constant to be

$$\begin{aligned} U_0 = &\sum_q F_{q0}\langle q_{q0}\rangle + \frac{1}{2!2}\sum_{q,r}\sum_{k_q} F_{qk_qrk_r}(\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle - \langle \bar{q}_{qk_q}\rangle\langle \bar{q}_{rk_r}\rangle) + \frac{1}{2!2}\sum_q\sum_{k_q} F_{q-k_qqk_q}(\langle q^2_{qk_q}\rangle + \langle \bar{q}^2_{qk_q}\rangle) \\ &+ \frac{1}{2!2}\sum_{q,r}\sum_{k_r} F_{q0r-k_rrk_r}\langle q_{q0}\rangle(\langle q^2_{rk_r}\rangle + \langle \bar{q}^2_{rk_r}\rangle) + \frac{1}{3!2^{3/2}}\sum_{q,r,s}\sum_{k_q,k_r} F_{qk_qrk_rsk_s}(\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle\langle q_{sk_s}\rangle - 3\langle q_{qk_q}\rangle\langle \bar{q}_{rk_r}\rangle\langle \bar{q}_{sk_s}\rangle) \\ &+ \frac{1}{2!2!2!2^2}\sum_{q,r}\sum_{k_q,k_r} F_{q-k_qqk_qr-k_rrk_r}(\langle q^2_{qk_q}\rangle + \langle \bar{q}^2_{qk_q}\rangle)(\langle q^2_{rk_r}\rangle + \langle \bar{q}^2_{rk_r}\rangle) + \frac{1}{4!2^2}\sum_{q,r,s,t}\sum_{k_q,k_r,k_s} F_{qk_qrk_rsk_stk_t}(\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle\langle q_{sk_s}\rangle\langle q_{tk_t}\rangle \\ &+ \langle \bar{q}_{qk_q}\rangle\langle \bar{q}_{rk_r}\rangle\langle \bar{q}_{sk_s}\rangle\langle \bar{q}_{tk_t}\rangle - 6\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle\langle \bar{q}_{sk_s}\rangle\langle \bar{q}_{tk_t}\rangle) + \ldots, \end{aligned} \tag{40}$$

where $\langle q_{qk_q}\rangle$ and $\langle q^2_{qk_q}\rangle$ are the short-hand notations of $\langle \zeta^{v_{qk_q}}_{qk_q}|q_{qk_q}|\zeta^{v_{qk_q}}_{qk_q}\rangle$ and $\langle \zeta^{v_{qk_q}}_{qk_q}|q^2_{qk_q}|\zeta^{v_{qk_q}}_{qk_q}\rangle$, respectively, and $\langle \bar{q}_{qk_q}\rangle$ and $\langle \bar{q}^2_{qk_q}\rangle$ are defined accordingly. It should be understood that the summations must exclude the mode pk_p because of Eq. (38). The second term in the right-hand side also excludes $q_{qk_q}=q_{rk_r}$ as it is included in the third term. This second term involves the summation over only k_q but not k_r because $F_{qk_qrk_r}$ vanishes unless $k_q+k_r=2n$ (n is an integer). The terms that involve odd numbers of $\bar{q}$ do not appear in this equation because it satisfies the antisymmetry relation, $\bar{q}_{q-k_q}=-\bar{q}_{qk_q}$, and the k summations are taken over the whole first BZ.

The right-hand side of Eq. (40) does not have consistent K dependence. The first term scales as $K^{1/2}$ because F_{q0} is a $K^{1/2}$ quantity and $\langle q_{q0}\rangle=\langle \zeta^{v}_{q0}|q_{q0}|\zeta^{v}_{q0}\rangle$ is independent of K. The second and third terms scale as K^1 because $F_{qk_qrk_r}$ has the K^0 dependence and the summation over k_q gives rise to the factor of K^1. In the same way, we find the K dependence of the fourth and fifth terms to be $K^{1/2}$ and $K^{3/2}$, respectively. The sixth and seventh terms with the quartic force constants scale as K^1 and K^2, respectively. To summarize, only the quadratic terms and the terms with quartic force constants of the type $F_{q-k_qqk_qr-k_rrk_r}$ display the correct K^1 dependence in U_0.

The fact that U_0 is a sum of terms with varied K dependence does not immediately mean that VSCF lacks size-extensivity. This is because the terms with nonphysical K dependence may be shown to vanish in the bulk ($K=\infty$) limit. The terms whose K dependence is $K^{1/2}$ or a weaker power of K become asymptotically negligible as compared with the size-extensive (K^1) terms. It should also be noticed that the other terms with nonphysical K dependence always involve the expectation values of odd powers of the normal coordinates in ζ. Therefore, if ζ can be shown to be symmetric (i.e., even or odd) with respect to the origin as is a harmonic-oscillator wave function centered at the equilibrium lattice structure, these terms also vanish by symmetry and the entire expression remains size-extensive (K^1) in the bulk limit. That ζ is a harmonic-oscillator wave function (but with a frequency differing from ω) is indeed the case under certain circumstances to be specified below.

The gradient in Eq. (39) is given by

$$\begin{aligned} U_1 = &\Delta_{k_p}F_{p0} + \frac{\Delta_{k_p}}{2!2}\sum_q\sum_{k_q} F_{p0q-k_qqk_q}(\langle q^2_{qk_q}\rangle + \langle \bar{q}^2_{qk_q}\rangle) \\ &+ \sum_q F_{pk_pqk_q}\langle q_{qk_q}\rangle + \frac{1}{2!2^{1/2}}\sum_{q,r}\sum_{k_q} F_{pk_pqk_qrk_r}(\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle \\ &- \langle \bar{q}_{qk_q}\rangle\langle \bar{q}_{rk_r}\rangle) + \frac{1}{3!2}\sum_{q,r,s}\sum_{k_q,k_r} F_{pk_pqk_qrk_rsk_s}(\langle q_{qk_q}\rangle\langle q_{rk_r}\rangle\langle q_{sk_s}\rangle \\ &- 3\langle q_{qk_q}\rangle\langle \bar{q}_{rk_r}\rangle\langle \bar{q}_{sk_s}\rangle) + \ldots, \end{aligned} \tag{41}$$

where q_{qk_q}, q_{rk_r}, and q_{sk_s} must differ from q_{pk_p}. The terms in the right-hand side scale as $K^{1/2}$, $K^{1/2}$, K^0, $K^{1/2}$, and K^1, respectively. Their sum, therefore, does not exhibit well-defined K dependence. The third and subsequent terms vanish by symmetry if ζ is a harmonic-oscillator wave function for the reason described above. The first term (F_{p0}) is zero at the equilibrium lattice structure, but the second term is not; it represents the leading-order anharmonic effect on the lattice structure (see below). Note that the cubic force constants that enter this important term have the form $F_{p0q-k_qqk_q}$. The VSCF method is not size-extensive unless the sum of the first two

terms ("VSCF gradient") vanishes for every in-phase coordinate (q_{p0}). This point will be expounded at the end of this subsection.

The quadratic force constant is expanded as

$$\frac{1}{2!}U_2 = \frac{1}{2!}F_{p-k_p pk_p}+\frac{1}{2!}\sum_q F_{p-k_p pk_p q0}\langle q_{q0}\rangle + \frac{1}{2!2!2}\sum_q\sum_{k_q} F_{p-k_p pk_p q-k_q qk_q}(\langle q_{qk_q}^2\rangle+\langle \bar{q}_{qk_q}^2\rangle) + \frac{1}{2!2!2}\sum_{q,r}\sum_{k_q} F_{p-k_p pk_p qk_q r-k_q}(\langle q_{qk_q}\rangle\langle q_{rk_q}\rangle + \langle \bar{q}_{qk_q}\rangle\langle \bar{q}_{rk_q}\rangle)+\cdots, \tag{42}$$

where q_{q0}, q_{qk_q}, and q_{rk_q} must differ from q_{pk_p}. U_2 does not scale consistently, either, as the second (cubic) term scales as $K^{-1/2}$ and differently from the other terms, which are K^0 quantities. However, the second term vanishes in the bulk limit, and the fourth term is also zero by symmetry if ζ is a harmonic-oscillator wave function.

The cubic and quartic force constants are given by

$$\frac{1}{3!}U_3 = \frac{1}{3!2^{1/2}}F_{pk_p pk_p pk_p}+\frac{1}{3!2}\sum_q F_{pk_p pk_p pk_p qk_q}\langle q_{qk_q}\rangle + \frac{1}{2!2}\sum_q F_{p-k_p pk_p pk_p q-k_p}\langle q_{qk_p}\rangle, \tag{43}$$

$$\frac{1}{4!}U_4 = \frac{1}{4!2}F_{pk_p pk_p pk_p pk_p}+\frac{1}{3!2}F_{p-k_p pk_p pk_p pk_p}+\frac{1}{2!2!2^2}F_{p-k_p pk_p p-k_p pk_p}. \tag{44}$$

These expressions exhibit the $K^{-1/2}$ and K^{-1} dependence, respectively, and thus vanish in the bulk limit. Generally, if we assume that ζ is a harmonic-oscillator wave function, we can show that the nth-order force constants in U decay as $K^{1-n/2}$ or more rapidly regardless of the highest order of the force constants present in V.

Let us now suppose that all VSCF gradients [the sum of the first two terms in the right-hand side of Eq. (41)] are made to vanish by choosing an appropriate lattice structure (see the next subsection). The force constants and normal coordinates are determined at this origin. With U_3 and U_4 vanishing asymptotically, U reduces to a canonical harmonic potential (with zero off-diagonal quadratic force constants) in these normal coordinates at $K=\infty$. Each modal ($\zeta_{pk_p}^{v}$ or $\bar{\zeta}_{pk_p}^{v}$) is therefore a harmonic-oscillator wave function along the corresponding normal coordinate but with a different (i.e., renormalized) frequency. The change in frequency occurs because U_2 has a contribution from the quartic force constants $F_{q-k_q qk_q r-k_r rk_r}$. The modal is centered at the lattice structure with which the normal coordinates are determined and hence the expectation value of an odd power of q_{pk_p} in $\zeta_{pk_p}^{v}$ is zero by symmetry. Hence, with this choice of the lattice structure and normal coordinates, the VSCF equations become asymptotically size-extensive.

Alternatively, one can maintain the equilibrium lattice structure as the origin (where V is at minimum and $F_{p0}=0$) and neglect cubic force constants, which also restores size-extensivity in VSCF. Under this approximation, $U_{pk_p}^{\mathbf{v}}$ again becomes a canonical, renormalized harmonic potential. A modal in this potential must be symmetric (even or odd) with respect to the origin, erasing all nonphysical terms in $U_{pk_p}^{\mathbf{v}}$.

Conversely, when nonzero VSCF gradients are retained in the equations, the size-extensivity of VSCF cannot be proven. A different perspective on the issue of size-extensivity of VSCF is provided in the Appendix on the basis of the additivity (or the lack thereof) of the energies of noninteracting subsystems in a supermolecule.[43]

D. Size-extensive self-consistent field theory

The foregoing discussion reveals that the VSCF equations are plagued with terms with nonphysical K dependence, which are, however, shown to vanish under some circumstances. It is desirable to restore strict size-extensivity in the equations by retaining only the nonvanishing terms in U's that have the correct K dependence. We introduce the following restricted form of a QFF:

$$V_{q\mathrm{VSCF}} = \frac{1}{2!2}\sum_p\sum_{k_p} F_{p-k_p pk_p}(q_{pk_p}^2+\bar{q}_{pk_p}^2) + \frac{1}{2!2!2!2^2}\sum_{p,q}\sum_{k_p,k_q} F_{p-k_p pk_p q-k_q qk_q} \times (q_{pk_p}^2+\bar{q}_{pk_p}^2)(q_{qk_q}^2+\bar{q}_{qk_q}^2) \tag{45}$$

$$= \frac{1}{2!}\sum_p{\sum_{k_p}}' F_{p-k_p pk_p}(q_{pk_p}^2+\bar{q}_{pk_p}^2) + \frac{1}{2!2!2!}\sum_{p,q}{\sum_{k_p,k_q}}' F_{p-k_p pk_p q-k_q qk_q} \times (q_{pk_p}^2+\bar{q}_{pk_p}^2)(q_{qk_q}^2+\bar{q}_{qk_q}^2), \tag{46}$$

where q_{pk_p} must differ from q_{qk_q} and it should understood that the factor of $2^{-1/2}$ associated with each appearance of q_{pk_p} or $\bar{q}_{pk_p}$ in Eq. (45) is replaced by unity when $k_p=0$. For this QFF, we can write the one-mode potential of VSCF that has the correct size-dependence as follows:

$$U_{q\mathrm{VSCF}}^{\mathbf{v}}(q_{pk_p}) = \langle \Phi_{pk_p}^{\mathbf{v}}|V_{q\mathrm{VSCF}}|\Phi_{pk_p}^{\mathbf{v}}\rangle = U_0^{q\mathrm{VSCF}}+\frac{1}{2!}U_2^{q\mathrm{VSCF}}q_{pk_p}^2, \tag{47}$$

with

$$U_0^{q\mathrm{VSCF}} = \frac{1}{2!}\sum_q{\sum_{k_p}}' F_{q-k_q qk_q}(\langle q_{qk_q}^2\rangle+\langle \bar{q}_{qk_q}^2\rangle) + \frac{1}{2!2!2!}\sum_{q,r}{\sum_{k_q,k_r}}' F_{q-k_q qk_q r-k_r rk_r}(\langle q_{qk_q}^2\rangle+\langle \bar{q}_{qk_q}^2\rangle) \times (\langle q_{rk_r}^2\rangle+\langle \bar{q}_{rk_r}^2\rangle) \tag{48}$$

and

$$\frac{1}{2!}U_2^{q\mathrm{VSCF}} = \frac{1}{2!}F_{p-k_p pk_p} + \frac{1}{2!2!}\sum_q {\sum_{k_q}}' F_{p-k_p pk_p q-k_q qk_q} \times (\langle q_{qk_q}^2\rangle + \langle \bar{q}_{qk_q}^2\rangle), \quad (49)$$

where q_{qk_q} and q_{rk_r} differ from q_{pk_p} and $q_{qk_q}=q_{rk_r}$ and $\bar{q}_{qk_q}=\bar{q}_{rk_r}$ are excluded from the summation in Eq. (48). Equation (47) is a sum of the size-extensive (K^1) constant and the size-intensive (K^0) quadratic function. The vibrational Schrödinger problem with this harmonic potential can be solved analytically to yield size-intensive transition energies that include the effects of anharmonicity due to $F_{p-k_p pk_p q-k_q qk_q}$. We call this method quartic VSCF or qVSCF (see also the methods of renormalized and self-consistent phonons).[44] The one-mode potential given above varies with all the other modals through the last term of Eq. (47), and therefore, the qVSCF equations [Eqs. (34)–(36)] must be solved self-consistently. The modal $\zeta_{qk_q}^{v_{qk_q}}(\zeta_{qk_q}^{\bar{v}_{qk_q}})$ is a harmonic-oscillator wave function in q_{pk_p} ($\bar{q}_{pk_p}$) but with a different frequency than that of $\eta_{qk_q}^{v_{qk_q}}(\eta_{qk_q}^{\bar{v}_{qk_q}})$. The total energy of the state $\mathbf{v}$ is the expectation value of the Hamiltonian with $V_{q\mathrm{VSCF}}$ in the qVSCF wave function and is written as

$$\begin{aligned} E_{q\mathrm{VSCF}}^{\mathbf{v}} = &-\frac{1}{2}\sum_p {\sum_{k_p}}' \left\langle \zeta_{pk_p}^{v_{pk_p}} \middle| \frac{\partial^2}{\partial q_{pk_p}^2} \middle| \zeta_{pk_p}^{v_{pk_p}} \right\rangle \\ &-\frac{1}{2}\sum_p {\sum_{k_p}}' \left\langle \zeta_{pk_p}^{\bar{v}_{pk_p}} \middle| \frac{\partial^2}{\partial \bar{q}_{pk_p}^2} \middle| \zeta_{pk_p}^{\bar{v}_{pk_p}} \right\rangle \\ &+\frac{1}{2!}\sum_p {\sum_{k_p}}' F_{p-k_p pk_p}(\langle q_{pk_p}^2\rangle + \langle \bar{q}_{pk_p}^2\rangle) \\ &+\frac{1}{2!2!2!}\sum_{p,q} {\sum_{k_p,k_q}}' F_{p-k_p pk_p q-k_q qk_q}(\langle q_{pk_p}^2\rangle + \langle \bar{q}_{pk_p}^2\rangle) \\ &\times(\langle q_{qk_q}^2\rangle + \langle \bar{q}_{qk_q}^2\rangle), \end{aligned} \quad (50)$$

where q_{pk_p} ($\bar{q}_{pk_p}$) must not coincide with q_{qk_q} ($\bar{q}_{pk_p}$). Each term in the right-hand side scales as K^1, and the sum is therefore strictly size-extensive. It should be evident that the sextic force constants of the type $F_{p-k_p pk_p q-k_q qk_q r-k_r rk_r}$ and analogous higher even-order force constants can also be included in a size-extensive fashion, defining sextic, octic, etc. VSCF methods.

As discussed in the previous subsection, the necessary condition for the size-extensivity of VSCF is that all VSCF gradients vanish. In qVSCF introduced above, such terms are excluded from $V_{q\mathrm{VSCF}}$ defined above so that the resulting equations are manifestly size-extensive. They are however related to an anharmonic correction to the lattice structure (more specifically to the atomic positions but not to the lattice constants). The anharmonic correction ($\tilde{q}_{p0}$) measured in the real normal coordinates of the first kind is the one at which the VSCF gradients vanish identically,

$$\left.\frac{\partial \tilde{U}_{q\mathrm{VSCF}}^{\mathbf{v}}(q_{p0})}{\partial q_{p0}}\right|_{q_{p0}=\bar{q}_{p0}} = 0, \quad (51)$$

with

$$\tilde{U}_{q\mathrm{VSCF}}^{\mathbf{v}}(q_{p0}) = \tilde{U}_0^{q\mathrm{VSCF}} + \tilde{U}_1^{q\mathrm{VSCF}} q_{p0} + \frac{1}{2!}\tilde{U}_2^{q\mathrm{VSCF}} q_{p0}^2. \quad (52)$$

The gradient of $\tilde{U}_{q\mathrm{VSCF}}^{\mathbf{v}}$ is given, according to Eq. (41), by

$$\tilde{U}_1^{q\mathrm{VSCF}} = F_{p0} + \frac{1}{2!}\sum_q {\sum_{k_q}}' F_{p0q-k_q qk_q}(\langle q_{qk_q}^2\rangle + \langle \bar{q}_{qk_q}^2\rangle), \quad (53)$$

whereas the expressions of $\tilde{U}_0^{q\mathrm{VSCF}}$ and $\tilde{U}_2^{q\mathrm{VSCF}}$ can be readily inferred from Eqs. (48) and (49), for instance,

$$\tilde{U}_2^{q\mathrm{VSCF}} = F_{p0p0} + \frac{1}{2!}\sum_q {\sum_{k_q}}' F_{p0p0q-k_q qk_q}(\langle q_{qk_q}^2\rangle + \langle \bar{q}_{qk_q}^2\rangle). \quad (54)$$

With these force constants, the anharmonic correction to the structure in the state $\mathbf{v}$ due to the cubic force constants of the type $F_{p0q-k_q qk_q}$ is

$$\tilde{q}_{p0} = -\tilde{U}_1^{q\mathrm{VSCF}}/\tilde{U}_2^{q\mathrm{VSCF}}. \quad (55)$$

Since $\tilde{U}_1^{q\mathrm{VSCF}}$ and $\tilde{U}_2^{q\mathrm{VSCF}}$ scale as $K^{1/2}$ and K^0, respectively, the anharmonic correction ($\tilde{q}_{p0}$) in the normal coordinate is a $K^{1/2}$ quantity. When expressed in spatially local coordinates such as the Cartesian coordinates, the correction $\tilde{X}_{\nu(0)}$ is given by

$$\tilde{X}_{\nu(0)} = K^{-1/2} m_\nu^{-1/2} \sum_p C_{p0}^{\nu *} \tilde{q}_{p0}, \quad (56)$$

which has the correct K^0 dependence.

Equation (55) can be evaluated approximately and expediently by using the harmonic-oscillator wave functions as modals, that is, $\langle q_{qk_q}\rangle \approx \langle \eta_{qk_q}^{v_{qk_q}} | q_{qk_q} | \eta_{qk_q}^{v_{qk_q}}\rangle$, and so forth. However, the fully self-consistent qVSCF procedure must simultaneously satisfy Eq. (51) to determine the lattice structure that ensures its size-extensivity and the VSCF equations with the potential given by Eq. (47). These two problems are coupled through the VSCF modals.

E. Perturbation theory

With a qVSCF wave function as the reference, the first- and second-order quartic VMP perturbation corrections to the energy ($E_{q\mathrm{VSCF}}^{\mathbf{v}}$) of the state $\mathbf{v}$ due to anharmonicity (denoted qVMP1 and qVMP2, respectively) are given by

$$E_{q\mathrm{VMP1}}^{\mathbf{v}} = E_{q\mathrm{VSCF}}^{\mathbf{v}} + \langle \Phi_{\mathrm{VSCF}}^{\mathbf{v}} | \tilde{V}_{q\mathrm{VSCF}} | \Phi_{\mathrm{VSCF}}^{\mathbf{v}}\rangle \quad (57)$$

and

$$E_{q\mathrm{VMP2}}^{\mathbf{v}} = E_{q\mathrm{VMP1}}^{\mathbf{v}} + \sum_{\mathbf{w}} \frac{|\langle \Phi_{\mathrm{VSCF}}^{\mathbf{v}} | \tilde{V}_{q\mathrm{VSCF}} | \Phi_{\mathrm{VSCF}}^{\mathbf{w}}\rangle|^2}{E_{q\mathrm{VSCF}}^{\mathbf{v}} - E_{q\mathrm{VSCF}}^{\mathbf{w}}}, \quad (58)$$

where the summation runs over all states $\mathbf{w}$ except for the state $\mathbf{v}$ and its degenerate states (if any). The operator $\tilde{V}_{q\mathrm{VSCF}}$ is the perturbation (the fluctuation potential) defined by the Møller–Plesset partitioning,[19–21]

$$\tilde{V}_{q\mathrm{VSCF}} = V - V_{q\mathrm{VSCF}}. \quad (59)$$

It should be recalled that under the assumption that makes VSCF size-extensive, namely, the first two terms of Eq. (41)

are zero or neglected, ζ becomes a harmonic-oscillator wave function centered at the origin (but not corresponding to $V_{\rm HRM}$). Therefore, the expectation value of an odd power of the normal coordinates in ζ vanishes by symmetry. In a QFF, therefore, we have

$$\langle \Phi^{\mathbf{v}}_{\rm VSCF} | \tilde{V}_{q\rm VSCF} | \Phi^{\mathbf{v}}_{\rm VSCF} \rangle = 0 \tag{60}$$

and

$$E^{\mathbf{v}}_{q\rm VMP1} = E^{\mathbf{v}}_{q\rm VSCF}, \tag{61}$$

which is size-extensive. That the reference modals are symmetric (even or odd) with respect to the origin ensures the disappearance of non-size-extensive terms involving F_{p0} and $F_{p0q-k_qqk_q}$.

The qVMP2 energy ($E^{\mathbf{v}}_{q\rm VMP2}$) is expressed as

$$\begin{aligned} E^{\mathbf{v}}_{q\rm VMP2} = E^{\mathbf{v}}_{q\rm VMP1} &+ \sum_{\mathbf{p}} \frac{|V^{v_{\mathbf{p}}}_{w_{\mathbf{p}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ &+ \frac{1}{2!} \sum_{\mathbf{p},\mathbf{q}} {\sum_{k_p}}' \frac{|V^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ &+ \frac{1}{3!} \sum_{\mathbf{p},\mathbf{q},\mathbf{r}} {\sum_{k_p,k_q}}' \frac{|V^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ &+ \frac{1}{4!} \sum_{\mathbf{p},\mathbf{q},\mathbf{r},\mathbf{s}} {\sum_{k_p,k_q,k_r}}' \frac{|V^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}v_{\mathbf{s}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}w_{\mathbf{s}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}}, \end{aligned} \tag{62}$$

where $\mathbf{p}$ is a compound index of p and k_p and corresponds to a member of the nonredundant set of normal coordinates of the first kind, namely, the union of $\{q_{pk_p}\}$ and $\{\bar{q}_{pk_p}\}$ in the half BZ. The k summations in the above expression are redundant as the summations over $\mathbf{p}$, $\mathbf{q}$, etc. imply them, but they are made explicit for the sake of clarifying the K dependence. The V matrix elements are defined by

$$V^{v_{\mathbf{p}}}_{w_{\mathbf{p}}} = \langle \Phi^{\mathbf{v}}_{q\rm VSCF} | \tilde{V}_{q\rm VSCF} | \Phi^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} \rangle, \tag{63}$$

$$V^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}} = \langle \Phi^{\mathbf{v}}_{q\rm VSCF} | \tilde{V}_{q\rm VSCF} | \Phi^{w_{\mathbf{p}}w_{\mathbf{q}}}_{v_{\mathbf{p}}v_{\mathbf{q}}} \rangle, \tag{64}$$

$$V^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}} = \langle \Phi^{\mathbf{v}}_{q\rm VSCF} | \tilde{V}_{q\rm VSCF} | \Phi^{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}}_{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}} \rangle, \tag{65}$$

and so forth, where $\Phi^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ denotes a one-mode excited qVSCF wave function in which the quantum number of the mode $\mathbf{p}$ is raised from $v_{\mathbf{p}}$ to $w_{\mathbf{p}}$. The modes $\mathbf{p}$, $\mathbf{q}$, $\mathbf{r}$, and $\mathbf{s}$ must be distinct from one another.

Of all $\mathbf{p}$'s, only those with $k_p=0$ can contribute to the second sum in the right-hand side of Eq. (62), that is,

$$\sum_{\mathbf{p}} \frac{|V^{v_{\mathbf{p}}}_{w_{\mathbf{p}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} = \sum_{p} \sum_{w_{pk_p}} \frac{|V^{v_{pk_p}}_{w_{pk_p}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}}, \tag{66}$$

with

$$\begin{aligned} V^{v_{pk_p}}_{w_{pk_p}} = {} & \Delta_{k_p} F_{p0} \langle \zeta^{v_{p0}}_{p0} | q_{p0} | \zeta^{w_{p0}}_{p0} \rangle \\ & + \frac{\Delta_{k_p}}{2!} \sum_{q} {\sum_{k_q}}' F_{p0q-k_qqk_q} \langle \zeta^{v_{p0}}_{p0} | q_{p0} | \zeta^{w_{p0}}_{p0} \rangle \\ & \times (\langle \zeta^{v_{qk_q}}_{qk_q} | q^2_{qk_q} | \zeta^{v_{qk_q}}_{qk_q} \rangle + \langle \zeta^{\bar{v}_{qk_q}}_{qk_q} | \bar{q}^2_{qk_q} | \zeta^{\bar{v}_{qk_q}}_{qk_q} \rangle). \end{aligned} \tag{67}$$

The first term in the right-hand side of Eq. (67) scales as $K^{1/2}$ because F_{p0} is a $K^{1/2}$ quantity. The other term also has the $K^{1/2}$ dependence because $F_{p0q-k_qqk_q}$ scales as $K^{-1/2}$ and the k summation gives rise to the factor of K^1. The numerator of Eq. (66) is therefore a K^1 quantity. The denominator is a qVSCF transition energy and is size-intensive (K^0). Overall, Eq. (66) scales correctly as K^1 and is size-extensive.

Remembering that $\mathbf{p}$ can stand for either q_{pk_p} or $\bar{q}_{pk_p}$, we find that the third term in the right-hand side of Eq. (62) consists of three sums,

$$\begin{aligned} & \frac{1}{2!} \sum_{\mathbf{p},\mathbf{q}} {\sum_{k_p}}' \frac{|V^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ & = \frac{1}{2!} \sum_{p,q} {\sum_{k_p}}' \sum_{w_{pk_p}, w_{qk_q}} \frac{|V^{v_{pk_p}v_{qk_q}}_{w_{pk_p}w_{qk_q}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ & + \frac{1}{2!} \sum_{p,q} {\sum_{k_p}}' \sum_{\bar{w}_{pk_p}, \bar{w}_{qk_q}} \frac{|V^{\bar{v}_{pk_p}\bar{v}_{qk_q}}_{\bar{w}_{pk_p}\bar{w}_{qk_q}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}} \\ & + \sum_{p,q} {\sum_{k_p}}' \sum_{w_{pk_p}, \bar{w}_{qk_q}} \frac{|V^{v_{pk_p}\bar{v}_{qk_q}}_{w_{pk_p}\bar{w}_{qk_q}}|^2}{E^{\mathbf{v}}_{q\rm VSCF} - E^{\mathbf{w}}_{q\rm VSCF}}, \end{aligned} \tag{68}$$

where

$$\begin{aligned} V^{v_{pk_p}v_{qk_q}}_{w_{pk_p}w_{qk_q}} = {} & \frac{1}{2} F_{pk_pqk_q} \langle \zeta^{v_{pk_p}}_{pk_p} | q_{pk_p} | \zeta^{w_{pk_p}}_{pk_p} \rangle \langle \zeta^{v_{qk_q}}_{qk_q} | q_{qk_q} | \zeta^{w_{qk_q}}_{qk_q} \rangle \\ & + \frac{1}{2!2} \sum_{r} {\sum_{k_r}}' F_{pk_pqk_qr-k_rrk_r} \langle \zeta^{v_{pk_p}}_{pk_p} | q_{pk_p} | \zeta^{w_{pk_p}}_{pk_p} \rangle \\ & \times \langle \zeta^{v_{qk_q}}_{qk_q} | q_{qk_q} | \zeta^{w_{qk_q}}_{qk_q} \rangle (\langle \zeta^{v_{rk_r}}_{rk_r} | q^2_{rk_r} | \zeta^{v_{rk_r}}_{rk_r} \rangle \\ & + \langle \zeta^{\bar{v}_{rk_r}}_{rk_r} | \bar{q}^2_{rk_r} | \zeta^{\bar{v}_{rk_r}}_{rk_r} \rangle), \end{aligned} \tag{69}$$

$$\begin{aligned} V^{v_{pk_p}\bar{v}_{qk_q}}_{w_{pk_p}\bar{w}_{qk_q}} = {} & \frac{i}{2} F_{pk_pqk_q} \langle \zeta^{v_{pk_p}}_{pk_p} | q_{pk_p} | \zeta^{w_{pk_p}}_{pk_p} \rangle \langle \zeta^{v_{qk_q}}_{qk_q} | \bar{q}_{qk_q} | \zeta^{w_{qk_q}}_{qk_q} \rangle \\ & + \frac{i}{2!2} \sum_{r} {\sum_{k_r}}' F_{pk_pqk_qr-k_rrk_r} \langle \zeta^{v_{pk_p}}_{pk_p} | q_{pk_p} | \zeta^{w_{pk_p}}_{pk_p} \rangle \\ & \times \langle \zeta^{v_{qk_q}}_{qk_q} | \bar{q}_{qk_q} | \zeta^{w_{qk_q}}_{qk_q} \rangle (\langle \zeta^{v_{rk_r}}_{rk_r} | q^2_{rk_r} | \zeta^{v_{rk_r}}_{rk_r} \rangle \\ & + \langle \zeta^{\bar{v}_{rk_r}}_{rk_r} | \bar{q}^2_{rk_r} | \zeta^{\bar{v}_{rk_r}}_{rk_r} \rangle). \end{aligned} \tag{70}$$

The definition of $V^{\bar{v}_{pk_p}\bar{v}_{qk_q}}_{\bar{w}_{pk_p}\bar{w}_{qk_q}}$ can be obtained by interchanging v with $\bar{v}$ and w with $\bar{w}$ in Eq. (69). Notice that $V^{v_{pk_p}\bar{v}_{qk_q}}_{w_{pk_p}\bar{w}_{qk_q}}$ contains terms with odd numbers of $\bar{q}$ and pure imaginary factors. In VMP2, these terms are squared before the k summa-

tion is taken and, therefore, can make nonvanishing contributions unlike in qVSCF. The two-mode V matrix elements scale as K^0, making Eq. (68) a K^1 quantity and size-extensive.

Likewise, the fourth term in Eq. (62) is an abbreviated notation of the sum of four terms,

$$\begin{aligned}
&\frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}}\sum_{k_p,k_q}{}' \frac{|V^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}}|^2}{E^{\mathbf{v}}_{q\mathrm{VSCF}}-E^{\mathbf{w}}_{q\mathrm{VSCF}}} \\
&= \frac{1}{3!}\sum_{p,q,r}\sum_{k_p,k_q}{}' \sum_{w_{pk_p},w_{qk_q},w_{rk_r}} \frac{|V^{v_{pk_p}v_{qk_q}v_{rk_r}}_{w_{pk_p}w_{qk_q}w_{rk_r}}|^2}{E^{\mathbf{v}}_{q\mathrm{VSCF}}-E^{\mathbf{w}}_{q\mathrm{VSCF}}} \\
&+ \frac{1}{3!}\sum_{p,q,r}\sum_{k_p,k_q}{}' \sum_{\bar{w}_{pk_p},\bar{w}_{qk_q},\bar{w}_{rk_r}} \frac{|V^{\bar{v}_{pk_p}\bar{v}_{qk_q}\bar{v}_{rk_r}}_{\bar{w}_{pk_p}\bar{w}_{qk_q}\bar{w}_{rk_r}}|^2}{E^{\mathbf{v}}_{q\mathrm{VSCF}}-E^{\mathbf{w}}_{q\mathrm{VSCF}}} \\
&+ \frac{1}{2!}\sum_{p,q,r}\sum_{k_p,k_q}{}' \sum_{w_{pk_p},\bar{w}_{qk_q},\bar{w}_{rk_r}} \frac{|V^{v_{pk_p}\bar{v}_{qk_q}\bar{v}_{rk_r}}_{w_{pk_p}\bar{w}_{qk_q}\bar{w}_{rk_r}}|^2}{E^{\mathbf{v}}_{q\mathrm{VSCF}}-E^{\mathbf{w}}_{q\mathrm{VSCF}}} \\
&+ \frac{1}{2!}\sum_{p,q,r}\sum_{k_p,k_q}{}' \sum_{w_{pk_p},w_{qk_q},\bar{w}_{rk_r}} \frac{|V^{v_{pk_p}v_{qk_q}\bar{v}_{rk_r}}_{w_{pk_p}w_{qk_q}\bar{w}_{rk_r}}|^2}{E^{\mathbf{v}}_{q\mathrm{VSCF}}-E^{\mathbf{w}}_{q\mathrm{VSCF}}},
\end{aligned} \tag{71}$$

where

$$\begin{aligned}
V^{v_{pk_p}v_{qk_q}v_{rk_r}}_{w_{pk_p}w_{qk_q}w_{rk_r}} &= \frac{1}{2^{3/2}}F_{pk_pqk_qrk_r}\langle\zeta^{v_{pk_p}}_{pk_p}|q_{pk_p}|\zeta^{w_{pk_p}}_{pk_p}\rangle \\
&\times\langle\zeta^{v_{qk_q}}_{qk_q}|q_{qk_q}|\zeta^{w_{qk_q}}_{qk_q}\rangle\langle\zeta^{v_{rk_r}}_{rk_r}|q_{rk_r}|\zeta^{w_{rk_r}}_{rk_r}\rangle,
\end{aligned} \tag{72}$$

$$\begin{aligned}
V^{v_{pk_p}v_{qk_q}\bar{v}_{rk_r}}_{w_{pk_p}w_{qk_q}\bar{w}_{rk_r}} &= \frac{i}{2^{3/2}}F_{pk_pqk_qrk_r}\langle\zeta^{v_{pk_p}}_{pk_p}|q_{pk_p}|\zeta^{w_{pk_p}}_{pk_p}\rangle \\
&\times\langle\zeta^{v_{qk_q}}_{qk_q}|q_{qk_q}|\zeta^{w_{qk_q}}_{qk_q}\rangle\langle\zeta^{\bar{v}_{rk_r}}_{rk_r}|\bar{q}_{rk_r}|\zeta^{\bar{w}_{rk_r}}_{rk_r}\rangle,
\end{aligned} \tag{73}$$

and so forth. These and other three-mode V matrix elements scale as $K^{-1/2}$. The numerators of Eq. (71) are therefore invariably K^{-1} quantities. Since the twofold k summation contributes the factor of K^2, we find Eq. (71) size-extensive also.

Generally, an n-mode V matrix element is a $K^{1-n/2}$ quantity just as is an nth-order force constant in the normal coordinates. With this knowledge, the fifth term in Eq. (62) with quartic force constants and thus the VMP2 correction as a whole can be shown to be size-extensive. Clearly, quintic, sextic, and all higher-order force constants can contribute to VMP2 in a size-extensive fashion, defining quintic, sextic, etc. VMP2 methods.

Alternatively, the harmonic-oscillator wave function $\Phi^{\mathbf{v}}_{\mathrm{HRM}}$ can be used as the reference. The first- and second-order perturbation corrections[45,46] to $E^{\mathbf{v}}_{\mathrm{HRM}}$ of the state $\mathbf{v}$ are given by

$$E^{\mathbf{v}}_{\mathrm{VPT1}} = E^{\mathbf{v}}_{\mathrm{HRM}} + \langle\Phi^{\mathbf{v}}_{\mathrm{HRM}}|\tilde{V}_{\mathrm{HRM}}|\Phi^{\mathbf{v}}_{\mathrm{HRM}}\rangle \tag{74}$$

and

$$E^{\mathbf{v}}_{\mathrm{VPT2}} = E^{\mathbf{v}}_{\mathrm{VPT1}} + \sum_{\mathbf{w}}\frac{|\langle\Phi^{\mathbf{v}}_{\mathrm{HRM}}|\tilde{V}_{\mathrm{HRM}}|\Phi^{\mathbf{w}}_{\mathrm{HRM}}\rangle|^2}{E^{\mathbf{v}}_{\mathrm{HRM}}-E^{\mathbf{w}}_{\mathrm{HRM}}}, \tag{75}$$

where the summation runs over all states $\mathbf{w}$ except for the state $\mathbf{v}$ and its degenerate states. The operator $\tilde{V}_{\mathrm{HRM}}$ denotes the perturbation (the fluctuation potential) defined as

$$\tilde{V}_{\mathrm{HRM}} = V - V_{\mathrm{HRM}}. \tag{76}$$

When V is a QFF, we call this method quartic VPT1. Its energy, $E^{\mathbf{v}}_{q\mathrm{VPT1}}$, can be written simply as[45,46]

$$\begin{aligned}
E^{\mathbf{v}}_{q\mathrm{VPT1}} = E^{\mathbf{v}}_{\mathrm{HRM}} + \frac{1}{2!2!2!}\sum_{p,q}\sum_{k_p,k_q}{}' F_{p-k_ppk_pq-k_qqk_q}(\langle q^2_{pk_p}\rangle \\
+\langle\bar{q}^2_{pk_p}\rangle)(\langle q^2_{qk_q}\rangle+\langle\bar{q}^2_{qk_q}\rangle),
\end{aligned} \tag{77}$$

where q_{pk_p} ($\bar{q}_{pk_p}$) must differ from q_{qk_q} ($\bar{q}_{qk_q}$) and the integral $\langle q^2_{pk_p}\rangle$ is understood to designate $\langle\eta^{v_{pk_p}}_{pk_p}|q^2_{pk_p}|\eta^{v_{pk_p}}_{pk_p}\rangle$, which can be evaluated analytically (see Table 27 in Ref. 38 or Appendix III in Ref. 39). Quadratic force constants do not appear in this expression because of Eq. (76). No expectation values of odd powers of the normal coordinates enter them either because of symmetry. $E^{\mathbf{v}}_{\mathrm{VPT1}}$ is size-extensive (K^1) as $F_{p-k_ppk_pq-k_qqk_q}$ is a K^{-1} quantity, and the twofold k summation gives rise to the factor of K^2. This expression is consistent with the anharmonic correction in the qVSCF energy given by Eq. (50) and reduces to the latter exactly when the qVSCF modals (ζ's) coincide with the harmonic-oscillator wave functions (η's). As in VSCF, the sextic force constants of the type $F_{p-k_ppk_pq-k_qqk_qr-k_rrk_r}$ and higher even-order force constants can be included in VPT1 in a size-extensive fashion.

In a QFF, the second-order anharmonic correction [Eq. (75)] is expressed as

$$\begin{aligned}
E^{\mathbf{v}}_{q\mathrm{VPT2}} = E^{\mathbf{v}}_{q\mathrm{VPT1}} &+ \sum_{\mathbf{p}}\frac{|W^{v_{\mathbf{p}}}_{w_{\mathbf{p}}}|^2}{E^{\mathbf{v}}_{\mathrm{HRM}}-E^{\mathbf{w}}_{\mathrm{HRM}}} \\
&+ \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}}\sum_{k_p}{}'\frac{|W^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}}|^2}{E^{\mathbf{v}}_{\mathrm{HRM}}-E^{\mathbf{w}}_{\mathrm{HRM}}} \\
&+ \frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}}\sum_{k_p,k_q}{}'\frac{|W^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}}|^2}{E^{\mathbf{v}}_{\mathrm{HRM}}-E^{\mathbf{w}}_{\mathrm{HRM}}} \\
&+ \frac{1}{4!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r},\mathbf{s}}\sum_{k_p,k_q,k_r}{}'\frac{|W^{v_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}v_{\mathbf{s}}}_{w_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}w_{\mathbf{s}}}|^2}{E^{\mathbf{v}}_{\mathrm{HRM}}-E^{\mathbf{w}}_{\mathrm{HRM}}},
\end{aligned} \tag{78}$$

where the summations exclude terms with vanishing denominators. Each sum in the right-hand side can be expanded similarly as Eqs. (66), (68), and (71). Elements of the W matrices are defined by Eqs. (67), (69), (70), (72), and (73), etc., in which the qVSCF modals (ζ's) are systematically replaced by the harmonic-oscillator wave functions (η's). We call this method quartic VPT2 or qVPT2. Equation (18) can be used to simplify the denominators, which are size-intensive (K^0). It can be readily shown that each term in the right-hand side of Eq. (78) is size-extensive (K^1) by recognizing that an n-mode W matrix element scales as $K^{1-n/2}$ and

an n-fold k summation gives rise to the factor of K^n. In the second-order correction also, higher-order force constants can be included without impairing size-extensivity.

F. Configuration-interaction theory

A VCI wave function[22] of the state $\mathbf{v}$ in a QFF is a linear combination of the ground and excited qVSCF wave functions,

$$\Phi^{\mathbf{v}}_{q\mathrm{VCI}} = \Phi^{\mathbf{v}}_{q\mathrm{VSCF}} + \sum_{\mathbf{p}} C^{w_\mathbf{p}}_{v_\mathbf{p}} \Phi^{w_\mathbf{p}}_{v_\mathbf{p}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}} {\sum_{k_p}}' C^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} \Phi^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + \frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}} {\sum_{k_p,k_q}}' C^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} + \cdots . \tag{79}$$

The expansion can be truncated after the n-fold excited contribution, defining n-mode qVCI or qVCI(n). Substituting this wave function into the Schrödinger equation,

$$\hat{H}_\mathrm{n} \Phi^{\mathbf{v}}_{q\mathrm{VCI}} = E^{\mathbf{v}}_{q\mathrm{VCI}} \Phi^{\mathbf{v}}_{q\mathrm{VCI}}, \tag{80}$$

and requiring that it be satisfied within the same function space spanned by the qVSCF wave functions that are used to expand the qVCI wave function, we arrive at the qVCI equations to be solved for the unknown coefficients C's,

$$E^{\mathbf{v}}_{q\mathrm{VCI}} = E^{\mathbf{v}}_{q\mathrm{VSCF}} + \sum_{\mathbf{p}} V^{v_\mathbf{p}}_{w_\mathbf{p}} C^{w_\mathbf{p}}_{v_\mathbf{p}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}} {\sum_{k_p}}' V^{v_\mathbf{p} v_\mathbf{q}}_{w_\mathbf{p} w_\mathbf{q}} C^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + \cdots , \tag{81}$$

$$E^{\mathbf{v}}_{q\mathrm{VCI}} C^{w_\mathbf{p}}_{v_\mathbf{p}} = V^{w_\mathbf{p}}_{v_\mathbf{p}} + E^{w_\mathbf{p}}_{q\mathrm{VSCF}} C^{w_\mathbf{p}}_{v_\mathbf{p}} + \sum_{\mathbf{q}} V^{v_\mathbf{p} v_\mathbf{q}}_{w_\mathbf{p} w_\mathbf{q}} C^{w_\mathbf{q}}_{v_\mathbf{q}} + \sum_{\mathbf{r}} V^{v_\mathbf{r}}_{w_\mathbf{r}} C^{w_\mathbf{p} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{r}} + \frac{1}{2!}\sum_{\mathbf{q},\mathbf{r}} {\sum_{k_q}}' V^{w_\mathbf{p} v_\mathbf{q} v_\mathbf{r}}_{v_\mathbf{p} w_\mathbf{q} w_\mathbf{r}} C^{w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{q} v_\mathbf{r}} + \cdots , \tag{82}$$

$$E^{\mathbf{v}}_{q\mathrm{VCI}} C^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} = V^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + E^{w_\mathbf{p} w_\mathbf{q}}_{q\mathrm{VSCF}} C^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + \sum_{\mathbf{r}} V^{w_\mathbf{p} w_\mathbf{q} v_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} w_\mathbf{r}} C^{w_\mathbf{r}}_{v_\mathbf{r}} + \sum_{\mathbf{r}} V^{w_\mathbf{p} v_\mathbf{r}}_{v_\mathbf{p} w_\mathbf{r}} C^{w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{q} v_\mathbf{r}} + \sum_{\mathbf{r}} V^{w_\mathbf{q} v_\mathbf{r}}_{v_\mathbf{q} w_\mathbf{r}} C^{w_\mathbf{p} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{r}} + \cdots , \tag{83}$$

and so forth, where $\mathbf{p}$, $\mathbf{q}$, and $\mathbf{r}$ are distinct from one another and $E^{w_\mathbf{p}}_{q\mathrm{VSCF}}$ denotes the energy of the qVSCF wave function in which the quantum number of the mode $\mathbf{p}$ is raised from $v_\mathbf{p}$ to $w_\mathbf{p}$. The V matrix elements are defined by Eqs. (63)–(65) as well as by

$$V^{w_\mathbf{p}}_{v_\mathbf{p}} = \langle \Phi^{w_\mathbf{p}}_{v_\mathbf{p}} | \tilde{V}_{q\mathrm{VSCF}} | \Phi^{\mathbf{v}}_{q\mathrm{VSCF}} \rangle, \tag{84}$$

$$V^{w_\mathbf{p} v_\mathbf{q}}_{v_\mathbf{p} w_\mathbf{q}} = \langle \Phi^{w_\mathbf{p}}_{v_\mathbf{p}} | \tilde{V}_{q\mathrm{VSCF}} | \Phi^{w_\mathbf{q}}_{v_\mathbf{q}} \rangle, \tag{85}$$

$$V^{w_\mathbf{p} v_\mathbf{q} v_\mathbf{r}}_{v_\mathbf{p} w_\mathbf{q} w_\mathbf{r}} = \langle \Phi^{w_\mathbf{p}}_{v_\mathbf{p}} | \tilde{V}_{q\mathrm{VSCF}} | \Phi^{w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{q} v_\mathbf{r}} \rangle, \tag{86}$$

and so forth. They also scale as $K^{1-n/2}$, where n is the number of modes involved.

With this, we find it impossible to assign well-defined K dependence to C's. Let us examine the K dependence of Eq. (81). The left-hand side and the first term in the right-hand side are size-extensive (K^1) quantities. For the subsequent terms to be size-extensive, n-mode CI coefficients must scale as $K^{1-n/2}$. In this way, for instance, $V^{v_\mathbf{p} v_\mathbf{q}}_{w_\mathbf{p} w_\mathbf{q}}$ and $C^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}}$ in the second term both scale as K^0, and the summation over k_p gives rise to the factor of K^1, making the third term in the right-hand side overall size-extensive (K^1). Let us now consider Eq. (82). The left-hand side is a $K^{3/2}$ quantity because, according to the preceding analysis, $E^{\mathbf{v}}_{q\mathrm{VCI}}$ and $C^{w_\mathbf{p}}_{v_\mathbf{p}}$ scale as K^1 and $K^{1/2}$, respectively. This contradicts the $K^{1/2}$ dependence of the right-hand side except for the second term, which scales as $K^{3/2}$. Therefore, qVCI is not size-extensive. An analysis of Eq. (83) only reinforces this conclusion. Notice that the K dependence of the so-called "disconnected" terms is different and thus incompatible with that of "connected" terms; the disconnected terms, in this case, are the products of E, V, and/or C's with no common summation index such as the left-hand side of Eq. (82) and the second term in the right-hand side of the same.

G. Coupled-cluster theory

The VCC method introduced by Christiansen[23–26] is size-extensive (see also Refs. 47–50). An algebraic proof of this is given here on the basis of an analysis of the K dependence. A VCC wave function in a QFF (qVCC) with a qVSCF reference is written as

$$\Phi^{\mathbf{v}}_{q\mathrm{VCC}} = \Phi^{\mathbf{v}}_{q\mathrm{VSCF}} + \sum_{\mathbf{p}} T^{w_\mathbf{p}}_{v_\mathbf{p}} \Phi^{w_\mathbf{p}}_{v_\mathbf{p}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}} {\sum_{k_p}}' T^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} \Phi^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}} T^{w_\mathbf{p}}_{v_\mathbf{p}} T^{w_\mathbf{q}}_{v_\mathbf{q}} \Phi^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} + \frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}} {\sum_{k_p,k_q}}' T^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}} {\sum_{k_p}}' T^{w_\mathbf{p} w_\mathbf{q}}_{v_\mathbf{p} v_\mathbf{q}} T^{w_\mathbf{r}}_{v_\mathbf{r}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} + \frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r}} T^{w_\mathbf{p}}_{v_\mathbf{p}} T^{w_\mathbf{q}}_{v_\mathbf{q}} T^{w_\mathbf{r}}_{v_\mathbf{r}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} + \frac{1}{4!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r},\mathbf{s}} {\sum_{k_p,k_q,k_r}}' T^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r} w_\mathbf{s}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r} v_\mathbf{s}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r} w_\mathbf{s}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r} v_\mathbf{s}} + \frac{1}{3!}\sum_{\mathbf{p},\mathbf{q},\mathbf{r},\mathbf{s}} {\sum_{k_p,k_q}}' T^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r}} T^{w_\mathbf{s}}_{v_\mathbf{s}} \Phi^{w_\mathbf{p} w_\mathbf{q} w_\mathbf{r} w_\mathbf{s}}_{v_\mathbf{p} v_\mathbf{q} v_\mathbf{r} v_\mathbf{s}} + \cdots , \tag{87}$$

where T's are the unknown coefficients ("T amplitudes") determined by the equations to be discussed shortly. Again, $\mathbf{p}$, $\mathbf{q}$, $\mathbf{r}$, and $\mathbf{s}$ denote compound indices of distinct modes. The number of modes in T can be limited to n, defining n-mode qVCC or qVCC(n). This equation is distinguished from the qVCI counterpart [Eq. (79)] by the presence of the terms containing two or more T's such as the fourth term in the right-hand side. Therefore, $\Phi^{\mathbf{v}}_{q\mathrm{VCC}}$ has contributions from the qVSCF wave functions that are excited in as many modes as there are in the whole system (in this case, $3NK$).

The T amplitudes are determined by requiring that the qVCC wave function satisfy the Schrödinger equation,

$$\hat{H}_{\mathrm{n}}\Phi^{\mathbf{v}}_{q\mathrm{VCC}} = E^{\mathbf{v}}_{q\mathrm{VCC}}\Phi^{\mathbf{v}}_{q\mathrm{VCC}}, \tag{88}$$

within the space spanned by the qVSCF reference and its excited wave functions up to n modes. In this way, we have the same number of equations as unknowns, which includes the energy $E^{\mathbf{v}}_{q\mathrm{VCC}}$. For instance, the projections of Eq. (88) onto the qVSCF reference ($\Phi^{\mathbf{v}}_{q\mathrm{VSCF}}$) and one-mode excited wave functions lead to the so-called energy and T_1 amplitude equations, respectively, which read

$$E^{\mathbf{v}}_{q\mathrm{VCC}} = E^{\mathbf{v}}_{q\mathrm{VSCF}} + \sum_{\mathbf{p}} V^{v_{\mathbf{p}}}_{w_{\mathbf{p}}} T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}}{\sum_{k_p}}' V^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}} T^{w_{\mathbf{p}}w_{\mathbf{q}}}_{v_{\mathbf{p}}v_{\mathbf{q}}} + \frac{1}{2!}\sum_{\mathbf{p},\mathbf{q}} V^{v_{\mathbf{p}}v_{\mathbf{q}}}_{w_{\mathbf{p}}w_{\mathbf{q}}} T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}} + \cdots \tag{89}$$

and

$$\begin{aligned} E^{\mathbf{v}}_{q\mathrm{VCC}} T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} &= V^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} + E^{w_{\mathbf{p}}}_{q\mathrm{VSCF}} T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} + \sum_{\mathbf{q}} V^{w_{\mathbf{p}}v_{\mathbf{q}}}_{v_{\mathbf{p}}w_{\mathbf{q}}} T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}} \\ &+ \sum_{\mathbf{r}} V^{v_{\mathbf{r}}}_{w_{\mathbf{r}}} T^{w_{\mathbf{p}}w_{\mathbf{r}}}_{v_{\mathbf{p}}v_{\mathbf{r}}} + \sum_{\mathbf{r}} V^{v_{\mathbf{r}}}_{w_{\mathbf{r}}} T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} T^{w_{\mathbf{r}}}_{v_{\mathbf{r}}} \\ &+ \frac{1}{2!}\sum_{\mathbf{q},\mathbf{r}}{\sum_{k_q}}' V^{w_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{q}}w_{\mathbf{r}}}_{v_{\mathbf{q}}v_{\mathbf{r}}} \\ &+ \frac{1}{2!}\sum_{\mathbf{q},\mathbf{r}} V^{w_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}} T^{w_{\mathbf{r}}}_{v_{\mathbf{r}}} + \cdots . \end{aligned} \tag{90}$$

Note that the third term in the right-hand side of Eq. (89) has a summation over k_p while the subsequent (fourth) term does not. This is because $T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ vanishes unless the momentum conservation condition ($\Delta_{k_p}=0$) is satisfied.

Equation (89) or the energy equation is size-extensive. Remembering that the n-mode V matrix elements scale as $K^{1-n/2}$ and assuming (as in qVCI) that the n-mode qVCC coefficients (the T_n amplitudes) are also the $K^{1-n/2}$ quantities, we find that each term in Eq. (89) scales consistently as K^1. Therefore, the left-hand side ($E^{\mathbf{v}}_{q\mathrm{VCC}}$) is size-extensive ($K^1$).

The T_1 amplitude equation [Eq. (90)] is not manifestly size-extensive. This can be seen by comparing the left-hand side, which is a $K^{3/2}$ quantity as $E^{\mathbf{v}}_{q\mathrm{VCC}}$ and $T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ scale as K^1 and $K^{1/2}$, respectively, with the first term in the right-hand side ($V^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$), which exhibits the $K^{1/2}$ dependence. However, multiplying Eq. (89) with $T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ and subtracting it from Eq. (90), we can bring the latter in a manifestly size-extensive form as

$$\begin{aligned} (E^{\mathbf{v}}_{q\mathrm{VSCF}} - E^{w_{\mathbf{p}}}_{q\mathrm{VSCF}}) T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} &= V^{w_{\mathbf{p}}}_{v_{\mathbf{p}}} + \sum_{\mathbf{q}} V^{w_{\mathbf{p}}v_{\mathbf{q}}}_{v_{\mathbf{p}}w_{\mathbf{q}}} T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}} \\ &+ \sum_{\mathbf{r}} V^{v_{\mathbf{r}}}_{w_{\mathbf{r}}} T^{w_{\mathbf{p}}w_{\mathbf{r}}}_{v_{\mathbf{p}}v_{\mathbf{r}}} \\ &+ \frac{1}{2!}\sum_{\mathbf{q},\mathbf{r}}{\sum_{k_q}}' V^{w_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{q}}w_{\mathbf{r}}}_{v_{\mathbf{q}}v_{\mathbf{r}}} \\ &+ \frac{1}{2!}\sum_{\mathbf{q},\mathbf{r}} V^{w_{\mathbf{p}}v_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{p}}w_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}} T^{w_{\mathbf{r}}}_{v_{\mathbf{r}}} + \cdots . \end{aligned} \tag{91}$$

The right-hand side of this equation consists of connected terms only, that is, the sums of products of V and T's that share at least one common summation index. For instance, the fifth term in the right-hand side of Eq. (90) is disconnected as none of the indices of $T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ is a summation index; this term cannot be seen in Eq. (91). The size-extensivity of the above equation can be verified by inspection of each term. The factor in the left-hand side, $(E^{\mathbf{v}}_{q\mathrm{VSCF}} - E^{w_{\mathbf{p}}}_{q\mathrm{VSCF}})$, is a transition energy and size-intensive (K^0), whereas $T^{w_{\mathbf{p}}}_{v_{\mathbf{p}}}$ is assumed to be a $K^{1/2}$ quantity. The left-hand side, therefore, scales as $K^{1/2}$. The first term in the right-hand side is a $K^{1/2}$ quantity. The second term also displays the $K^{1/2}$ dependence because $V^{w_{\mathbf{p}}v_{\mathbf{q}}}_{v_{\mathbf{p}}w_{\mathbf{q}}}$ and $T^{w_{\mathbf{q}}}_{v_{\mathbf{q}}}$ scale as K^0 and $K^{1/2}$, respectively. In this way, all terms can be shown to scale consistently as $K^{1/2}$.

The T_2 amplitude equation is obtained by the projection of Eq. (88) on to two-mode excited qVSCF wave functions ($\Phi^{w_{\mathbf{p}}w_{\mathbf{q}}}_{v_{\mathbf{p}}v_{\mathbf{q}}}$). They can furthermore be recast into the manifestly size-extensive, connected form as

$$\begin{aligned} (E^{\mathbf{v}}_{q\mathrm{VSCF}} - E^{w_{\mathbf{p}}w_{\mathbf{q}}}_{q\mathrm{VSCF}}) T^{w_{\mathbf{p}}w_{\mathbf{q}}}_{v_{\mathbf{p}}v_{\mathbf{q}}} &= V^{w_{\mathbf{p}}w_{\mathbf{q}}}_{v_{\mathbf{p}}v_{\mathbf{q}}} + \sum_{\mathbf{r}} V^{w_{\mathbf{p}}w_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{p}}v_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{r}}}_{v_{\mathbf{r}}} + \sum_{\mathbf{r}} V^{w_{\mathbf{p}}v_{\mathbf{r}}}_{v_{\mathbf{p}}w_{\mathbf{r}}} T^{w_{\mathbf{q}}w_{\mathbf{r}}}_{v_{\mathbf{q}}v_{\mathbf{r}}} \\ &+ \sum_{\mathbf{r}} V^{w_{\mathbf{q}}v_{\mathbf{r}}}_{v_{\mathbf{q}}w_{\mathbf{r}}} T^{w_{\mathbf{p}}w_{\mathbf{r}}}_{v_{\mathbf{p}}v_{\mathbf{r}}} + \cdots . \end{aligned} \tag{92}$$

It can be readily shown that each term in this equation consistently scales as K^0 using the fact that the n-mode V matrix elements and T_n amplitudes both scale as $K^{1-n/2}$. This procedure can be repeated for T_3 and higher-order T amplitude equations, proving the size-extensivity of qVCC.

Higher-order force constants can be included in VCC without impairing the size-extensivity or the need for adjusting the VSCF reference wave function accordingly. VCC can also be defined analogously for the harmonic-oscillator reference wave function by simply replacing the V matrix elements by the corresponding W matrix elements and $E^{\mathbf{v}}_{q\mathrm{VSCF}}$ by their harmonic counterparts. VCC remains size-extensive after these replacements.

IV. CONCLUSIONS

The issue of size-extensivity of vibrational many-body methods has been analyzed on the basis of the dependence of terms in their formalisms on the number (K) of k vectors in the first BZ, which is a measure of the system size. The aim has been to make these methods applicable to anharmonic lattice vibrations in solids. Taking a one-dimensional solid with a QFF PES as an example, the compact and strictly size-extensive equations of VSCF have been proposed, introducing the qVSCF method. It accounts for the effect of anharmonicity due to quartic force constants of the type $F_{p-k_p pk_p q-k_q qk_q}$ on the transition energies and that due to cubic force constants of the type $F_{p0q-k_q qk_q}$ on the lattice structures. Size-extensive VMP1, VMP2, and VCC in a QFF have been defined with the qVSCF wave function as the reference by elucidating the K scaling of integrals and excitation amplitudes. Size-extensive VPT1 and VPT2 in a QFF using the harmonic-oscillator reference wave function have also been considered. These methods and the conclusions about their

size-extensivity can be readily generalized to two- and three-dimensional solids as well as to a Taylor expansion of PES truncated at any arbitrary order. This analysis, however, cannot be applied to a grid representation of PES. An algebraic proof of the lack of size-extensivity in VCI has also been given.

This article concentrates on these formal aspects, specifically the structure of size-extensive vibrational many-body methods for anharmonic lattice vibrations. A computer implementation of the proposed methods is underway in our laboratory and will be reported in separate articles.

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APPENDIX: NONINTERACTING DIATOMIC MOLECULES

Let us consider a VSCF treatment of a supermolecule consisting of $K=2^m$ noninteracting, identical diatomic molecules (m is a positive integer). Let q_i be the internal coordinate (bond length) of the ith molecule. These coordinates are therefore spatially localized on the individual molecules. The QFF PES of the supermolecule can be expressed in these local coordinates as

$$V(q_1, \ldots, q_K) = \sum_i V_i(q_i), \tag{A1}$$

with

$$V_i(q_i) = E + F_1 q_i + F_2 q_i^2 + F_3 q_i^3 + F_4 q_i^4, \tag{A2}$$

where E is the energy of a molecule at the origin and F_n is the nth-order force constant. This PES is size-extensive (K^1) as it sums the potentials of the K molecules. The one-mode potential of VSCF for the internal coordinate q_i is then given by

$$\begin{aligned} U_i(q_i) = KE + \sum_{j\neq i} (&F_1\langle\zeta_j|q_j|\zeta_j\rangle + F_2\langle\zeta_j|q_j^2|\zeta_j\rangle \\ &+ F_3\langle\zeta_j|q_j^3|\zeta_j\rangle + F_4\langle\zeta_j|q_j^4|\zeta_j\rangle) + F_1 q_i + F_2 q_i^2 \\ &+ F_3 q_i^3 + F_4 q_i^4, \end{aligned} \tag{A3}$$

where ζ_j is a VSCF modal of q_j. This one-mode potential is the sum of size-extensive constants (the first two terms) and size-intensive functions of q_i. It is identical to the QFF of the isolated molecule (V_i) apart from some constant. If the VSCF equations [Eq. (34)] are solved with these one-mode potentials, one trivially obtains the same modals as those of the isolated molecules. The total energy, which is an expectation value of the Hamiltonian in the product of ζ_i's, is K times the energy of the isolated molecule and, therefore, exact. This is simply the consequence of the fact that virtually any many-body method can be made size-extensive in a spatially localized basis.[3] Although a local-basis approach to anharmonic lattice vibrations is an important subject of research, the issue of size-extensivity is pertinent to the methods that employ thoroughly delocalized bases such as normal coordinates.

Since the harmonic-oscillator wave functions along the internal coordinates q_i's are degenerate, one is free to apply a unitary transformation to them and define a new set of coordinates that are delocalized over the entire supermolecule. One such set can be defined by

$$Q_i = K^{-1/2}\sum_j H_{ij} q_j, \tag{A4}$$

where H is the Kth-order Hadamard matrix in Sylvester's construction. It has the property, $K^{-1}HH^T=I$, where I is the identity matrix. Its element is either $+1$ or -1, and each column or row of the matrix has the same numbers $(K/2)$ of positive $(+1)$ and negative (-1) entries except for the first column and row, which have only positive $(+1)$ entries.

Using these relationships, the potential V is expressed in the delocalized coordinates Q's as

$$\begin{aligned} V(Q_1, \ldots, Q_K) = KE + K^{1/2}F_1 Q_1 + F_2\sum_i Q_i^2 + K^{-1/2}F_3 Q_1^3 \\ + 3K^{-1/2}F_3\sum_{i\neq 1} Q_i^2 Q_1 + K^{-1}F_4\sum_i Q_i^4 \\ + 6K^{-1}F_4\sum_{j>i} Q_j^2 Q_i^2, \end{aligned} \tag{A5}$$

where Q_1 corresponds to the in-phase stretching vibrations of all K molecules. Note that the nth-order force constants are multiplied by the factor of $K^{1-n/2}$ as expected from the foregoing analysis [Eqs. (25)–(28)]. The one-mode potentials of VSCF along Q_1 and Q_i $(i>1)$ are written as

$$\begin{aligned} U_1(Q_1) = \tilde{U}_1 + K^{1/2}F_1 Q_1 + F_2 Q_1^2 + K^{-1/2}F_3 Q_1^3 \\ + 3K^{-1/2}F_3\sum_{j\neq 1}\langle\zeta_j|Q_j^2|\zeta_j\rangle Q_1 + K^{-1}F_4 Q_1^4 \\ + 6K^{-1}F_4\sum_{j\neq 1}\langle\zeta_j|Q_j^2|\zeta_j\rangle Q_1^2, \end{aligned} \tag{A6}$$

$$\begin{aligned} U_i(Q_i) = \tilde{U}_i + F_2 Q_i^2 + 3K^{-1/2}F_3\langle\zeta_1|Q_1|\zeta_1\rangle Q_i^2 + K^{-1}F_4 Q_i^4 \\ + 6K^{-1}F_4\sum_{j\neq i}\langle\zeta_j|Q_j^2|\zeta_j\rangle Q_i^2, \end{aligned} \tag{A7}$$

where ζ_j is the VSCF modal of Q_j and $\tilde{U}_1$ and $\tilde{U}_i$ $(i>1)$ are the constants

$$\begin{aligned} \tilde{U}_1 = KE + F_2\sum_{j\neq 1}\langle\zeta_j|Q_j^2|\zeta_j\rangle + K^{-1}F_4\sum_{j\neq 1}\langle\zeta_j|Q_j^4|\zeta_j\rangle \\ + 6K^{-1}F_4\sum_{k>j,j\neq 1}\langle\zeta_k|Q_k^2|\zeta_k\rangle\langle\zeta_j|Q_j^2|\zeta_j\rangle, \end{aligned} \tag{A8}$$

$$\tilde{U}_i = KE + F_2 \sum_{j\neq i} \langle \zeta_j | Q_j^2 | \zeta_j \rangle + K^{-1} F_4 \sum_{j\neq i} \langle \zeta_j | Q_j^4 | \zeta_j \rangle + 6K^{-1} F_4 \sum_{k>j, j\neq i, k\neq i} \langle \zeta_k | Q_k^2 | \zeta_k \rangle \langle \zeta_j | Q_j^2 | \zeta_j \rangle + K^{1/2} F_1 \langle \zeta_1 | Q_1 | \zeta_1 \rangle + K^{-1/2} F_3 \langle \zeta_1 | Q_1^3 | \zeta_1 \rangle + 3K^{-1/2} F_3 \sum_{j\neq i, j\neq 1} \langle \zeta_1 | Q_1 | \zeta_1 \rangle \langle \zeta_j | Q_j^2 | \zeta_j \rangle. \quad \text{(A9)}$$

Neither of these potentials agrees with Eq. (A3), and therefore, the VSCF equations of the supermolecule in this delocalized set of coordinates will have different solutions from those of the isolated molecule. This has been confirmed numerically for a noninteracting hydrogen fluoride dimer. Furthermore, U_1 and U_i $(i>1)$ differ from each other and the degeneracy will be lifted, which has also been observed numerically for the dimer.

This entails two related but separate issues. First, the VSCF wave functions and energies are not invariant to a unitary transformation of coordinates. The lack of invariance in VSCF is known.[51] It means that VSCF is ill-defined unless the coordinates used are precisely specified. This may pose a particularly serious problem when there are degenerate normal modes because such normal modes are not uniquely determined by Eq. (10).

Second, the one-mode potentials of VSCF do not have the correct size dependence. The lack of size-extensivity is caused primarily by the presence of F_1 and F_3. It is reasonable to require that $F_1=0$, that is, the coordinates be centered at the equilibrium structure of the supermolecule. If F_3, furthermore, happens to vanish or is neglected, U restores size-extensivity because Eqs. (A6) and (A7) both reduce to

$$U_i(Q_i) = KE + F_2 \sum_{j\neq i} \langle \zeta_j | Q_j^2 | \zeta_j \rangle + 6K^{-1} F_4 \sum_{k>j, j\neq i, k\neq i} \langle \zeta_k | Q_k^2 | \zeta_k \rangle \langle \zeta_j | Q_j^2 | \zeta_j \rangle + F_2 Q_i^2 + 6K^{-1} F_4 \sum_{j\neq i} \langle \zeta_j | Q_j^2 | \zeta_j \rangle Q_i^2, \quad \text{(A10)}$$

asymptotically, from which the terms that scale as K^0 and K^{-1} and therefore vanish in the bulk limit have been removed. The first three terms, which are constant, are size-extensive; the sums in the second and third terms scale as K and K^2, respectively. It can be understood similarly that the last two terms, which are functions of Q_i, are size-intensive. Overall, therefore, Eq. (A10) has the correct size dependence. This one-mode potential has the same structure as the qVSCF one-mode potential [Eq. (47)] as it should. It does not yield the same modal or transition energies as Eq. (A2) and (A3), nor does the total energy equal K times the energy of the isolated molecule. However, this is due to the lack of invariance rather than to the lack of size-extensivity.

It should be evident from this discussion that the supermolecule criteria of size-extensivity[43] are not equivalent to the more rigorous K-dependence criteria adopted in the rest of this article. The one-mode potential of Eq. (A10) is size-extensive according to the K-dependence criteria, but it does not satisfy the supermolecule criteria because of the lack of invariance.

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