Analytical evaluation of energy derivatives in extended systems. I. Formalism

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A method is developed to analytically evaluate energy derivatives for extended systems. Linear dependence among basis functions, which almost always occurs in extended systems and brings instability to the coupled-perturbed equations, is automatically eliminated in this method. The remaining independent basis functions are transformed into semiorthogonal orbitals. The derivatives of the orbitals and the overlap matrix over them are obtained via a set of coupled-perturbed equations, similar to those of the coupled-perturbed Hartree-Fock (CPHF) equations which are used to calculate the derivatives of the Hartree-Fock (HF) orbitals and the orbital energies. By introducing symmetrized coordinates, these coupled-perturbed equations can be easily solved. Explicit expressions for calculating gradients and Hessians of the HF energy for extended systems are given. With this method, we can calculate energy derivatives with respect to displacements of the nuclei, including those which break the translational symmetry. Therefore, the method not only provides an efficient and accurate approach to calculate energy derivatives of any order, but also enables us to determine the force constants for individual nuclei, the interatomic force constants, and phonon dispersion curves in the whole Brillouin zone. With this method, the computational cost to calculate phonon spectrum with $\mathbf{k}\neq 0$ in the Brillouin zone is the same as that needed for the spectrum at $\mathbf{k}=0$. © *1998 American Institute of Physics.* [S0021-9606(98)30635-2]

I. INTRODUCTION

The analytical evaluation of energy derivatives is one of the most important achievements of quantum chemistry.[1–3] It not only provides accurate results but also is much more efficient than a numerical, finite difference method. After 30 years of development, analytical gradients and Hessians have become routine for various self-consistent field (SCF) methods and the most widely used correlated methods, although this is still one of the most active fields in quantum chemistry.[4–11]

The analytical evaluation of energy derivatives has been mainly confined to finite systems. Nevertheless, some substantial progress has been made in the last several years. With the STO-3G basis set, Teramae *et al.*[12] calculated the analytical gradients of the HF energy for several polymers under the constraint that all unit cells are moving in phase. Under the same constraint, Hirata and Iwata[13] have calculated the analytical gradients of the density functional theory (DFT) energy for polyacetylene (with a 3-21G basis set) and polymethineimine (with 3-21G and 6-31G* basis sets). Recently, two groups[14–16] have calculated the phonon dispersion curves (with analytical Hessians) for several semiconductors and aluminum using DFT with plane wave basis functions, which do not depend on the geometry of the nuclei. Using plane wave functions as the basis set, the calculations can be greatly simplified, and some problems associated with extended systems can be avoided, but it is very difficult to get converged results, especially for insulators and semiconductors. So far, to our knowledge, no one has systematically studied the analytical evaluation of energy derivatives (gradients, Hessians, and higher orders) for a general (typically Gaussian) basis set without constraints on the movement of nuclei.

The analytical evaluation of energy derivatives for extended systems is more complicated than that for finite molecules. There are at least two reasons for this: linear dependence among basis functions and infinite coupling when translational symmetry is broken. The former either makes the coupled-perturbed Hartree-Fock (CPHF) or alternative methods insoluble or causes large errors. It also invalidates the currently widely used formulas for analytical gradients, even though the solutions of the CPHF equations are not required.[17] This problem occasionally occurs in molecules. In most cases, one avoids the problem by simply replacing one basis set with another. But almost all the basis sets (except minimal basis sets such as STO-3G) tend to have linear dependencies when applied to polymers, and this problem will be worse for three dimensional systems. The latter of the two difficulties involves the design of an effective procedure to solve the CPHF equations for a general case. The translational symmetry of a periodic system no longer exists whenever a nucleus moves, no matter how small the displacement is. Without the periodicity, the Fock matrix is no longer block diagonal and the HF orbitals cannot be classified according to a reciprocal lattice vector $\mathbf{k}$. Then neither the Hartree-Fock (HF) nor the corresponding CPHF equations can be solved practically.

The analytical evaluation of energy derivatives is even more significant and necessary for extended systems than for finite molecules. First, the computational effort needed for an energy evaluation of an extended system with an *ab initio* method is much greater than that for a finite molecule. The analytical method for energy derivatives can greatly reduce the computational cost compared to finite difference procedures. It is also more reliable and accurate. Second, all *ab initio* methods applied to calculate the energy of an extended system require translational symmetry, and so the finite difference method can only provide energy derivatives with respect to displacements which maintain the symmetry. Therefore, one can only calculate the frequencies of the phonons at the Γ point. One may move to other special points in the first Brillouin zone by enlarging the unit cell of the system (the so called ''super cell'') and then calculate the frequencies of the phonon at these points.[18,19] But this is very expensive and the method is still an approach which requires translational symmetry. Therefore, with the finite difference method, it is very difficult to calculate the whole phonon dispersion curves and other properties involving the derivatives with respect to the displacements which break the translational symmetry. The phonon dispersion curves of a solid determine the system's specific heat, thermal conductivity, thermal expansion, infrared and Raman spectroscopy, and other mechanical properties.[19–21] Currently, the HF method has become routine for energies and band structures for extended systems[22–25] and recently second-order many-body perturbation theory [MBPT(2)][26] has been applied to calculate the vibrational frequencies of polymethineimine for the normal modes with $\mathbf{k=0}$, i.e., keeping the translational symmetry.[27] Clearly, the next step is to formulate an effective procedure for the analytical evaluation of energy derivatives in extended systems.

In the method, we propose that there are no special requirements for basis functions and no constraints for the displacements of the nuclei. The basis functions can be functions of the nuclei's coordinates and they may have linear dependence. A procedure, recently developed by us,[17] is used to automatically eliminate the linear dependence among basis functions and transform the remaining independent functions into a set of semiorthogonal orbitals. The procedure also provides the derivatives of the obtained orbitals and their overlap matrix. To effectively solve the CPHF equations, symmetrized coordinates for nuclei are used. They are Fourier transformations of the displacements of the nuclei and complex variables. The symmetrized coordinates are classified by a reciprocal vector $\mathbf{k}$ in the first Brillouin zone. Those with $\mathbf{k}=0$ do not break translational symmetry, while others do. We will show that with the symmetrized coordinates, both the coupled-perturbed equations for independent orbitals and the CPHF equations can be greatly simplified and then they can be easily solved. The CPHF equations for symmetrized coordinates with $\mathbf{k}\neq 0$ do not require more computational effort to be solved than those for $\mathbf{k}=0$, e.g., the phonon spectrum at any $\mathbf{k}$ point in the first Brillouin zone can be calculated with the same amount of computational cost as that required at the Γ point ($\mathbf{k}=0$, keeping translational symmetry). We will derive the detailed formulas for analytical gradients and Hessians of the HF energy. For completeness, we will also show how to calculate the force constants for individual nuclei, interatomic force constants, and the whole phonon dispersion curves in the first Brillouin zone using the Hessians.

The plan of this paper is as follows. In Sec. II, we will deal with basis functions to get independent, semiorthogonal orbitals and their derivatives. In Sec. III, we will give a general discussion about HF and CPHF equations for extended systems. In Sec. IV, we will simplify the coupled-perturbed equations for both semiorthogonal basis functions and HF orbitals using symmetrized coordinates for nuclei. In Sec. V, we will give the detailed expressions for analytical gradients and Hessians for the HF energy. Then we will discuss the applications of the energy derivatives in Sec. VI. In Sec. VII, we will close with concluding remarks.

II. INDEPENDENT BASIS FUNCTIONS

A. Symmetric and orthogonal orbitals for periodic systems

Let us consider a ρ-dimensional periodic, infinite system with basic vectors $\mathbf{a}_1,\ldots,\mathbf{a}_\rho$ (ρ=1,2,3). Then the position vector of the Ath nucleus in the lth unit cell is

$$\mathbf{R}_{lA}=\mathbf{R}_l+\mathbf{R}_A\,, \tag{1}$$

where

$$\mathbf{R}_l=l_1\mathbf{a}_1+\cdots+l_\rho\mathbf{a}_\rho \tag{2}$$

is the lattice vector for the lth unit cell and $\mathbf{R}_A$ is a position vector for the Ath nucleus in a unit cell. Let $\{\chi_\alpha^l(\mathbf{r})=\chi_\alpha(\mathbf{r}-\mathbf{R}_{lA}),l=0,\pm 1,\ldots\}$ be the atomic basis set. Then symmetrized or Bloch orbitals are given by

$$\phi_{\mathbf{k}\alpha}(\mathbf{r})=\frac{1}{\sqrt{\mathcal{N}}}\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\chi_\alpha^l(\mathbf{r}), \tag{3}$$

where $\mathcal{N}=\mathcal{N}_1,\ldots,\mathcal{N}_\rho$ is the number of the unit cells in the system and $\mathcal{N}_1,\ldots,\mathcal{N}_\rho$ can all go to infinity. The vector $\mathbf{k}$ in Eq. (3) is the reciprocal lattice $\mathbf{k}$ given by

$$\mathbf{k}=k_1\mathbf{b}_1+\cdots+k_\rho\mathbf{b}_\rho\,, \tag{4}$$

where $\mathbf{b}_1,\ldots,\mathbf{b}_\rho$ are defined by

$$\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}\,,\quad i,j=1,\ldots,\rho, \tag{5}$$

and k_i ($i=1,\ldots,\rho$) in Eq. (4) can only take values of the multiple of $2\pi/\mathcal{N}_i(i=1,\ldots,\rho)$, limited in the region of $[-\pi,\pi]$.[22–26]

The overlap matrix over the symmetrized orbitals is block diagonal, e.g.,

$$\mathbf{S}=\begin{pmatrix}\ddots & 0 & 0\\ 0 & \mathbf{S}^{\mathbf{k}} & 0\\ 0 & 0 & \ddots\end{pmatrix}, \tag{6}$$

where

$$S_{\alpha\beta}^{\mathbf{k}}=\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle\chi_\alpha^0|\chi_\beta^l\rangle. \tag{7}$$

The dimension of $\mathbf{S}^{\mathbf{k}}$ is equal to T, the number of atomic orbitals in one unit cell. It is easy to see that each $\mathbf{S}^{\mathbf{k}}$ is a Hermitian matrix. Then one can always find a unitary matrix $\mathbf{V}^{\mathbf{k}}$ such that

$$\mathbf{S}^{\mathbf{k}}\mathbf{V}^{\mathbf{k}}=\mathbf{V}^{\mathbf{k}}\mathbf{s}^{\mathbf{k}}, \tag{8}$$

where $\mathbf{s}^{\mathbf{k}}$ is a diagonal matrix,

$$\mathbf{s}^{\mathbf{k}}=\begin{pmatrix} \lambda_1^{\mathbf{k}} & 0 & \cdots & 0 \\ 0 & \lambda_2^{\mathbf{k}} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdot & \lambda_T^{\mathbf{k}} \end{pmatrix}, \tag{9}$$

and $\lambda_1^{\mathbf{k}} \geqslant \lambda_2^{\mathbf{k}} \geqslant \cdots \geqslant \lambda_T^{\mathbf{k}}$. For a small $\lambda_i^{\mathbf{k}}$, the corresponding one-particle wave function is considered to be dependent on the others and it should be discarded.[25] It is impossible to give an absolute value for λ to distinguish independent and dependent orbitals; nevertheless, one can choose a reasonably small value as a threshold according to the demanded accuracy of the calculation and throw away the basis functions whose eigenvalues are smaller than the chosen threshold. Then only $M^{\mathbf{k}}$ ($M^{\mathbf{k}} \leqslant T$) orthogonal functions from the T atomic orbitals can be constructed by

$$\overline{\phi_{\mathbf{k}\mu}}(\mathbf{r})=\sum_{\alpha}^{T} \phi_{\mathbf{k}\alpha}(\mathbf{r}) V_{\alpha\mu}^{\mathbf{k}}, \mu=1,\ldots,M^{\mathbf{k}}. \tag{10}$$

Since the atomic orbitals in one unit cell are exactly the same as those in any other unit cell, except that their origins are shifted by a lattice vector, the number of the dependent functions among each group of the symmetrized orbitals with the same $\mathbf{k}$ should not be a function of $\mathbf{k}$; that is, $M^{\mathbf{k}}$ is a constant. Of course, it may happen that $M^{\mathbf{k}}$ varies with $\mathbf{k}$ if the threshold is not well chosen. In this case, one must adjust it to be sure that the discarded orbitals are the same for all $\mathbf{k}$. This means one can find a universal M which preserves the number of orthogonal orbitals obtained for each $\mathbf{k}$.

It is easy to see from Eq. (7) that

$$(\mathbf{S}^{\mathbf{k}})^{*}=\mathbf{S}^{-\mathbf{k}}. \tag{11}$$

This means that

$$(\mathbf{s}^{\mathbf{k}})^{*}=\mathbf{s}^{-\mathbf{k}} \tag{12}$$

and also means that one can always have

$$(\mathbf{V}^{\mathbf{k}})^{*}=\mathbf{V}^{-\mathbf{k}}. \tag{13}$$

Let us use $\mathbf{V}_1^{\mathbf{k}}$ and $\mathbf{V}_2^{\mathbf{k}}$ to denote the first M columns and the remainder of $\mathbf{V}^{\mathbf{k}}$, respectively, and define

$$\mathbf{V}_1=\begin{pmatrix} \ddots & 0 & 0 \\ 0 & \mathbf{V}_1^{\mathbf{k}} & 0 \\ 0 & 0 & \ddots \end{pmatrix}, \tag{14}$$

$$\mathbf{V}_2=\begin{pmatrix} \ddots & 0 & 0 \\ 0 & \mathbf{V}_2^{\mathbf{k}} & 0 \\ 0 & 0 & \ddots \end{pmatrix}. \tag{15}$$

The matrix $\mathbf{V}_1$ transforms the atomic orbitals into independent, orthogonal orbitals, e.g.,

$$\{\ldots,\overline{\phi_{\mathbf{k}\mu}},\ldots\}=\{\ldots,\phi_{\mathbf{k}\mu},\ldots\}\mathbf{V}_1. \tag{16}$$

Let us use $\mathbf{s}_1^{\mathbf{k}}$ and $\mathbf{s}_2^{\mathbf{k}}$ to denote the top-left $M\times M$ square and the bottom-right $(T-M)\times(T-M)$ square of $\mathbf{s}^{\mathbf{k}}$, respectively, and define

$$\mathbf{s}_1=\begin{pmatrix} \ddots & 0 & 0 \\ 0 & \mathbf{s}_1^{\mathbf{k}} & 0 \\ 0 & 0 & \ddots \end{pmatrix}, \tag{17}$$

$$\mathbf{s}_2=\begin{pmatrix} \ddots & 0 & 0 \\ 0 & \mathbf{s}_2^{\mathbf{k}} & 0 \\ 0 & 0 & \ddots \end{pmatrix}. \tag{18}$$

It is easy to see that $\mathbf{s}_1$ is the overlap matrix over the orthogonal orbitals. With the above definitions, Eq. (8) can be rewritten in a more compact form as

$$\mathbf{SV}=\mathbf{Vs}, \tag{19}$$

where

$$\mathbf{V}=(\mathbf{V}_1,\mathbf{V}_2), \tag{20}$$

$$\mathbf{s}=\begin{pmatrix} \mathbf{s}_1 & 0 \\ 0 & \mathbf{s}_2 \end{pmatrix}. \tag{21}$$

B. Semisymmetric and independent orbitals for nonperiodic systems

Now let the nuclei have small displacements from the periodic structure, e.g.,

$$\mathbf{R}_{lA}=\mathbf{R}_l+\mathbf{R}_A+\Delta\mathbf{R}_{lA}, \tag{22}$$

where $\Delta\mathbf{R}_{lA}$ is a function of both l and A. Then there is no translational symmetry anymore. Nevertheless, we can still construct a set of semisymmetrized orbitals by

$$\phi_{\mathbf{k}\alpha}(y,\mathbf{r})=\frac{1}{\sqrt{\mathcal{N}}}\sum_{l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\chi_{\alpha}^{l}(y,\mathbf{r}), \tag{23}$$

where

$$\chi_{\alpha}^{l}(y,\mathbf{r})=\chi_{\alpha}(\mathbf{r}-\mathbf{R}_l-\mathbf{R}_A-\Delta\mathbf{R}_{lA}) \tag{24}$$

and y is used to denote the displacements of the nuclei, e.g., $y=\{\ldots,y_t,\ldots\}=\{\ldots,y_{lA\tau},\ldots\}=\{\ldots,\Delta R_{lA1}, 1\Delta R_{lA2},\Delta R_{lA3},\ldots\}$. It is easy to see that the semisymmetric and atomic orbitals are connected by a unitary matrix. Then they span the same function space and, of course, are equivalent. When $y=0$, semisymmetrical orbitals become identical to their corresponding symmetrized orbitals given in Eq. (3). It is known that the atomic orbitals are smooth functions of $\Delta\mathbf{R}_{lA}$, and so are the semisymmetrized orbitals since they are functions of the nuclei's coordinates only through the atomic orbitals. The overlap matrix of the orbitals can be calculated by

$$S_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)=\frac{1}{\mathcal{N}}\sum_{l'l} e^{i(\mathbf{k}\cdot\mathbf{R}_l-\mathbf{k}'\cdot\mathbf{R}_{l'})}\langle\chi_{\alpha'}^{l'}(y,\mathbf{r})|\chi_{\alpha}^{l}(y,\mathbf{r})\rangle, \tag{25}$$

which is no longer a block diagonal matrix except at $y=0$. When $y=0$, the overlap matrices given in Eqs. (7) and (25) become identical.

For $y \neq 0$, we can still find a unitary matrix, which is a smooth function of y, to transform the semisymmetrized orbitals into orthogonal ones. Then we can get $\mathcal{N}M$ independent orthogonal basis functions. Any rotation among the independent or dependent orbitals, respectively, does not change the space spanned by the independent basis functions. Let $\mathbf{V}(y)$ be a unitary matrix which satisfies

$$\mathbf{S}(y)\mathbf{V}(y)=\mathbf{V}(y)\mathbf{s}(y), \tag{26}$$

with the constraint that

$$\mathbf{s}(y)=\begin{pmatrix} \mathbf{s}_1(y) & \mathbf{0} \\ \mathbf{0} & \mathbf{s}_2(y) \end{pmatrix}. \tag{27}$$

$\mathbf{s}_1(y)$ and $\mathbf{s}_2(y)$ become identical to $\mathbf{s}_1$ and $\mathbf{s}_2$, respectively, when $y=0$. From the first $\mathcal{N}M$ columns of $\mathbf{V}(y)$, we can get $\mathcal{N}M$ independent basis functions by

$$\overline{\phi}_{\mathbf{k}\mu}(y,\mathbf{r})=\sum_{\mathbf{k}'\alpha} \phi_{\mathbf{k}'\alpha}(y,\mathbf{r})V_{\mathbf{k}'\alpha,\mathbf{k}\mu}, \quad \mu \leq M. \tag{28}$$

The symbol $\mathbf{k}$ in Eq. (28) only means that $\overline{\phi}_{\mathbf{k}\mu}(y,\mathbf{r})$ smoothly approaches $\overline{\phi}_{\mathbf{k}\mu}(\mathbf{r})$ when $y \to 0$.

C. Derivatives of the independent basis functions and their overlap matrix

Let us express $\mathbf{S}(y)$, $\mathbf{V}(y)$, and $\mathbf{s}(y)$ as Taylor series in the vicinity of $\mathbf{y}=0$,

$$\mathbf{S}(y)=\mathbf{S}+\sum_t \mathbf{S}^t y_t+\tfrac{1}{2}\sum_{t,t'} \mathbf{S}^{tt'} y_t y_{t'}+\cdots, \tag{29}$$

$$\mathbf{V}(y)=\mathbf{V}+\sum_t \mathbf{V}^t y_t+\tfrac{1}{2}\sum_{t,t'} \mathbf{V}^{tt'} y_t y_{t'}+\cdots, \tag{30}$$

$$\mathbf{s}(y)=\mathbf{s}+\sum_t \mathbf{s}^t y_t+\tfrac{1}{2}\sum_{t,t'} \mathbf{s}^{tt'} y_t y_{t'}+\cdots \quad . \tag{31}$$

For any derivative matrix, $\mathbf{V}^{tt'\cdots}$, of the coefficients, there is always a matrix $\mathbf{A}^{tt'\cdots}$ such that

$$\mathbf{V}^{tt'\cdots}=\mathbf{V}\mathbf{A}^{tt'\cdots}, \tag{32}$$

since $\mathbf{V}$ is a nonsingular square matrix. Substituting Eqs. (29)–(32) into Eq. (26), we can get[17]

$$\mathbf{s}^t+\mathbf{A}^t\mathbf{s}-\mathbf{s}\mathbf{A}^t=\mathbf{V}^\dagger\mathbf{S}^t\mathbf{V} \tag{33}$$

for first derivatives and

$$\mathbf{s}^{tt'}+\mathbf{A}^{tt'}\mathbf{s}-\mathbf{s}\mathbf{A}^{tt'}=\mathbf{V}^\dagger\mathbf{S}^{tt'}\mathbf{V}+\mathbf{s}^{t'}\mathbf{A}^t-\mathbf{A}^t\mathbf{s}^{t'}+\mathbf{s}^t\mathbf{A}^{t'}-\mathbf{A}^{t'}\mathbf{s}^t \\ +\mathbf{A}^{t'}\mathbf{s}\mathbf{A}^t+\mathbf{A}^t\mathbf{s}\mathbf{A}^{t'}-s\mathbf{A}^t\mathbf{A}^{t'}-s\mathbf{A}^{t'}\mathbf{A}^t \tag{34}$$

for second derivatives.

Among the matrices which satisfy Eqs. (26) and (27), we can always find one such that[17]

$$\mathbf{A}^t=\begin{pmatrix} \mathbf{0} & \mathbf{A}_{12}^t \\ -(\mathbf{A}_{12}^t)^\dagger & \mathbf{0} \end{pmatrix} \tag{35}$$

and

$$\mathbf{A}^{tt'}=\begin{pmatrix} \tfrac{1}{2}(\mathbf{A}_{12}^t\mathbf{A}_{21}^{t'}+\mathbf{A}_{12}^{t'}\mathbf{A}_{21}^t) & \mathbf{A}_{12}^{tt'} \\ -(\mathbf{A}_{12}^{tt'})^\dagger & \tfrac{1}{2}(\mathbf{A}_{21}^t\mathbf{A}_{12}^{t'}+\mathbf{A}_{21}^{t'}\mathbf{A}_{12}^t) \end{pmatrix}. \tag{36}$$

Substituting Eq. (35) into Eq. (33), we obtain

$$\mathbf{s}^t=\begin{pmatrix} \mathbf{V}_1^\dagger\mathbf{S}^t\mathbf{V}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{V}_2^\dagger\mathbf{S}^t\mathbf{V}_2 \end{pmatrix}, \tag{37}$$

$$A_{\mathbf{k}\mu,\mathbf{k}'\mu'}^t=\frac{1}{\lambda_{\mathbf{k}'\mu'}-\lambda_{\mathbf{k}\mu}}(\mathbf{V}^\dagger\mathbf{S}^t\mathbf{V})_{\mathbf{k}\mu,\mathbf{k}'\mu'}, \quad \mu \leq M;\mu'>M. \tag{38}$$

We can also substitute Eq. (36) into Eq. (34) and then get

$$s_{\mathbf{k}\mu,\mathbf{k}'\mu'}^{tt'}=[\mathbf{V}_1^\dagger\mathbf{S}^{tt'}\mathbf{V}_1+\mathbf{A}_{12}^t\mathbf{s}_2\mathbf{A}_{21}^{t'}+\mathbf{A}_{12}^{t'}\mathbf{s}_2\mathbf{A}_{21}^t \\ -\tfrac{1}{2}(\mathbf{A}_{12}^{t'}\mathbf{A}_{21}^t+\mathbf{A}_{12}^t\mathbf{A}_{21}^{t'})\mathbf{s}_1 \\ -\tfrac{1}{2}\mathbf{s}_1(\mathbf{A}_{12}^{t'}\mathbf{A}_{21}^t+\mathbf{A}_{12}^t\mathbf{A}_{21}^{t'})]_{\mathbf{k}\mu,\mathbf{k}'\mu'}, \quad \mu,\mu' \leq M, \tag{39}$$

$$A_{\mathbf{k}\mu,\mathbf{k}'\mu'}^{tt'}=\frac{1}{\lambda_{\mathbf{k}'\mu'}-\lambda_{\mathbf{k}\mu}}[\mathbf{V}_1^\dagger\mathbf{S}^{tt'}\mathbf{V}_2-\mathbf{A}_{12}^t\mathbf{s}_2^{t'}-\mathbf{A}_{12}^{t'}\mathbf{s}_2^t+\mathbf{s}_1^t\mathbf{A}_{12}^{t'} \\ +\mathbf{s}_1^{t'}\mathbf{A}_{12}^t]_{\mathbf{k}\mu,\mathbf{k}'\mu'}, \quad \mu \leq M;\mu'>M. \tag{40}$$

Now we have transformed the $\mathcal{N}T$ basis functions into $\mathcal{N}M$ independent, semiorthogonal orbitals and have derived the formulas to determine the derivatives of these orbitals and their overlap matrix.

III. HARTREE-FOCK AND COUPLED-PERTURBED HARTREE-FOCK FORMALISM

A. Hartree-Fock equations

With the basis functions $\{\overline{\phi}_{\mathbf{k}\mu}(y,\mathbf{r})\}$, one electron spatial wave functions can be expressed as

$$\psi_P(y,\mathbf{r})=\sum_{\mathbf{k}}\sum_{\mu=1}^{M} \overline{\phi}_{\mathbf{k}\mu}(y,\mathbf{r})D_{\mathbf{k}\mu,P}(y) \\ =\sum_{\mathbf{k}'}\sum_{\alpha=1}^{T} \phi_{\mathbf{k}'\alpha}(y,\mathbf{r})C_{\mathbf{k}'\alpha,P}(y), \tag{41}$$

where

$$C_{\mathbf{k}'\alpha,P}(y)=\sum_{\mathbf{k}}\sum_{\mu=1}^{M} V_{\mathbf{k}'\alpha,\mathbf{k}\mu}(y)D_{\mathbf{k}\mu,P}(y) \tag{42}$$

or

$$\mathbf{C}(y)=\mathbf{V}_1(y)\mathbf{D}(y). \tag{43}$$

The Fock matrix over the semiorthogonal orbitals, $\overline{\phi}_{\mathbf{k}\mu}(y,\mathbf{r})$, can be calculated by

$$\mathbf{F}(y)=\mathbf{V}_1^\dagger(y)\mathbf{F}'(y)\mathbf{V}_1(y), \tag{44}$$

where $\mathbf{F}'(y)$ is the Fock matrix over semisymmetrized orbitals, $\phi_{\mathbf{k}\mu}(y,\mathbf{r})$. In a semiconductor or an insulator, each occupied orbital always has two electrons in the ground state. The $\mathbf{F}'(y)$ can then be expressed as

$$F'_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)=h_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)+2J_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)-K_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y), \tag{45}$$

where

$$h_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)=\left\langle \phi_{\mathbf{k}'\alpha'}\left| -\tfrac{1}{2}\nabla^2 - \sum_{l,A}\frac{Z_A}{|\mathbf{r}-\mathbf{R}_l-\mathbf{R}_A-\Delta\mathbf{R}_{lA}|}\right|\phi_{\mathbf{k}\alpha}\right\rangle, \tag{46}$$

$$J_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)=\sum_I \langle \phi_{\mathbf{k}'\alpha'}\psi_I|r_{12}^{-1}|\phi_{\mathbf{k}\alpha}\psi_I\rangle, \tag{47}$$

$$K_{\mathbf{k}'\alpha',\mathbf{k}\alpha}(y)=\sum_I \langle \phi_{\mathbf{k}'\alpha'}\psi_I|r_{12}^{-1}|\psi_I\phi_{\mathbf{k}\alpha}\rangle \tag{48}$$

are matrices of one-particle, Coulomb, and exchange interactions, respectively. The summation index I in Eqs. (47) and (48) and in the following is limited to occupied spatial orbitals. The Hartree-Fock equation for the system is

$$\mathbf{F}(y)\mathbf{D}(y)=\mathbf{s}_1(y)\mathbf{D}(y)\epsilon(y), \tag{49}$$

$$\mathbf{D}^\dagger(y)\mathbf{s}_1(y)\mathbf{D}(y)=\mathbf{I}. \tag{50}$$

The HF energy for the system can be calculated by

$$E^{\mathrm{HF}}=\sum_I [\mathbf{D}^\dagger\mathbf{V}_1^\dagger\mathbf{h}\mathbf{V}_1\mathbf{D}+\mathbf{D}^\dagger\mathbf{F}\mathbf{D}]_{II}+V_{\mathrm{nuc}} =\sum_I [\mathbf{C}^\dagger\mathbf{h}\mathbf{C}+\mathbf{C}^\dagger\mathbf{F}'\mathbf{C}]_{II}+V_{\mathrm{nuc}}, \tag{51}$$

where V_{nuc} is the nuclear repulsion energy given by

$$V_{\mathrm{nuc}}=\tfrac{1}{2}\sum_{l,A,l',A'}{}' \frac{Z_AZ_B}{|\mathbf{R}_{lA}-\mathbf{R}_{l'A'}|}. \tag{52}$$

The prime on the summation in Eq. (52) means that the case where $l=l'$ and $A=A'$ is excluded.

When $y=0$, e.g., $\Delta\mathbf{R}_{lA}=0$ for all l and A, the translational symmetry insures $\mathbf{D}$ to be block diagonal,

$$\mathbf{D}=\begin{pmatrix} \ddots & 0 & 0\\ 0 & \mathbf{D}^{\mathbf{k}} & 0\\ 0 & 0 & \ddots \end{pmatrix} \tag{53}$$

and the HF orbitals to be Bloch functions,

$$\psi_{p\mathbf{k}}(\mathbf{r})=\sum_\mu \overline{\phi}_{\mathbf{k}\mu}(\mathbf{r})D^{\mathbf{k}}_{\mu p}. \tag{54}$$

Then the Fock matrices $\mathbf{F}'$ and $\mathbf{F}$ both become block diagonal too, e.g.,

$$\mathbf{F}=\begin{pmatrix} \ddots & 0 & 0\\ 0 & \mathbf{F}^{\mathbf{k}} & 0\\ 0 & 0 & \ddots \end{pmatrix}, \tag{55}$$

$$\mathbf{F}'=\begin{pmatrix} \ddots & 0 & 0\\ 0 & \mathbf{F}'^{\mathbf{k}} & 0\\ 0 & 0 & \ddots \end{pmatrix}, \tag{56}$$

where $\mathbf{F}^{\mathbf{k}}$ and $\mathbf{F}'^{\mathbf{k}}$ are connected by

$$\mathbf{F}^{\mathbf{k}}=(\mathbf{V}_1^{\mathbf{k}})^\dagger\mathbf{F}'^{\mathbf{k}}\mathbf{V}_1^{\mathbf{k}}. \tag{57}$$

Same as for independent orbitals, one can always have[22–25]

$$(\epsilon_{p\mathbf{k}})^*=\epsilon_{p(-\mathbf{k})}, \tag{58}$$

$$(\mathbf{D}^{\mathbf{k}})^*=\mathbf{D}^{-\mathbf{k}}. \tag{59}$$

With translational symmetry, Eqs. (45)–(48) become[22–25]

$$F'^{\mathbf{k}}_{\alpha\beta}=\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}[h^l_{\alpha\beta}+2J^l_{\alpha\beta}-K^l_{\alpha\beta}], \tag{60}$$

$$h^l_{\alpha\beta}=\int \chi^0_\alpha(\mathbf{r})\{-\tfrac{1}{2}\nabla^2\}\chi^l_\beta(\mathbf{r})d\mathbf{r} -\sum_{\mathbf{R}_h,A}\int \chi^0_\alpha(\mathbf{r})\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A-\mathbf{R}_h|}\chi^l_\beta(\mathbf{r})d\mathbf{r}, \tag{61}$$

$$J^l_{\alpha\beta}=\sum_{hh'\gamma\theta}\mathcal{D}^{hh'}_{\gamma\theta}(\chi^0_\alpha\chi^l_\beta|\chi^h_\gamma\chi^{h'}_\theta), \tag{62}$$

$$K^l_{\alpha\beta}=\sum_{hh'\gamma\theta}\mathcal{D}^{hh'}_{\gamma\theta}(\chi^0_\alpha\chi^{h'}_\theta|\chi^l_\beta\chi^h_\gamma), \tag{63}$$

where

$$(\chi^0_\alpha\chi^l_\beta|\chi^h_\gamma\chi^{h'}_\theta)=\int\int \chi^0_\alpha(\mathbf{r})\chi^l_\beta(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1} \times\chi^h_\gamma(\mathbf{r}')\chi^{h'}_\theta(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}', \tag{64}$$

$$\mathcal{D}^{hh'}_{\alpha\beta}=\frac{1}{\mathcal{W}}\sum_i \int d\mathbf{k}(C^{\mathbf{k}}_{\alpha i})^*C^{\mathbf{k}}_{\beta i}e^{i\mathbf{k}\cdot(\mathbf{R}_{h'}-\mathbf{R}_h)}. \tag{65}$$

The integration region over reciprocal lattice in Eq. (65) is defined in Sec. II A and $\mathcal{W}$ is its volume. The summation index i is limited to occupied bands. In the following, i, j, i', j' and a, b will be used to denote occupied and unoccupied bands, respectively, while p, q denote either.

B. Coupled-perturbed Hartree-Fock equations

Expressing $\mathbf{F}(y)$, $\mathbf{s}_1(y)$, and $\mathbf{D}(y)$ as Taylor series, we get

$$\mathbf{F}(y)=\mathbf{F}+\sum_t \mathbf{F}^t y_t+\sum_{tt'}\mathbf{F}^{tt'}y_ty_{t'}+\cdots, \tag{66}$$

$$\mathbf{s}_1(y)=\mathbf{s}_1+\sum_t \mathbf{s}_1^t y_t+\sum_{tt'}\mathbf{s}_1^{tt'}y_ty_{t'}+\cdots, \tag{67}$$

$$\mathbf{D}(y)=\mathbf{D}+\sum_t \mathbf{D}^t y_t+\sum_{tt'} \mathbf{D}^{tt'} y_t y_{t'}+\cdots . \tag{68}$$

As for the derivatives of the matrix $\mathbf{V}$, we can write

$$\mathbf{D}^{tt'\cdots}=\mathbf{D}\mathbf{U}^{tt'\cdots}. \tag{69}$$

From Eqs. (49) and (50), we get

$$(\mathbf{U}^t)^\dagger+\mathbf{U}^t=-\mathbf{D}^\dagger \mathbf{s}_1^t \mathbf{D}, \tag{70}$$

$$\boldsymbol{\epsilon}^t+\mathbf{U}^t\boldsymbol{\epsilon}-\boldsymbol{\epsilon}\mathbf{U}^t=\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}-\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D}\boldsymbol{\epsilon} \tag{71}$$

for first derivatives. As for finite systems, $\mathbf{U}^t$ can always be expressed as

$$\mathbf{U}^t=\mathbf{P}^t+\mathbf{Q}^t, \tag{72}$$

where $\mathbf{P}^t$ and $\mathbf{Q}^t$ are Hermitian and anti-Hermitian matrices, respectively. From Eq. (70), we get

$$\mathbf{P}^t=-\tfrac{1}{2}\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D}. \tag{73}$$

By rotating among occupied and unoccupied orbitals, respectively, one can always write[17,28]

$$\mathbf{Q}^t=\begin{pmatrix} \mathbf{0} & \mathbf{Q}_{12}^t \\ \mathbf{Q}_{21}^t & \mathbf{0} \end{pmatrix}, \tag{74}$$

while keeping matrix $\boldsymbol{\epsilon}^t$ block diagonal, e.g.,

$$\boldsymbol{\epsilon}^t=\begin{pmatrix} \boldsymbol{\epsilon}_1^t & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon}_2^t \end{pmatrix}. \tag{75}$$

Then the equations become

$$\begin{aligned}\epsilon^t_{p\mathbf{k}_p,q\mathbf{k}_q}&=[\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}-\tfrac{1}{2}(\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D}\boldsymbol{\epsilon}+\boldsymbol{\epsilon}\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D})]_{p\mathbf{k}_p,q\mathbf{k}_q}\\ &=[\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}-\tfrac{1}{2}(\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C}\boldsymbol{\epsilon}+\boldsymbol{\epsilon}\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C})]_{p\mathbf{k}_p,q\mathbf{k}_q},\\ &\quad p,q\leqslant n \quad or \quad p,q>n,\end{aligned} \tag{76}$$

$$\begin{aligned}Q^t_{a\mathbf{k}_a,i\mathbf{k}_i}&=-(Q^t_{i\mathbf{k}_i,a\mathbf{k}_a})^*\\ &=\frac{1}{\epsilon_{i\mathbf{k}_i}-\epsilon_{a\mathbf{k}_a}}\left[\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}-\frac{1}{2}(\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D}\boldsymbol{\epsilon}+\boldsymbol{\epsilon}\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D})\right]_{a\mathbf{k}_a,i\mathbf{k}_i}\\ &=\frac{1}{\epsilon_{i\mathbf{k}_i}-\epsilon_{a\mathbf{k}_a}}\left[\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}-\frac{1}{2}(\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C}\boldsymbol{\epsilon}+\boldsymbol{\epsilon}\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C})\right]_{a\mathbf{k}_a,i\mathbf{k}_i},\end{aligned} \tag{77}$$

where n is the number of the occupied bands.[22–26] The Fock matrix over HF orbitals, e.g., $\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}$, can be calculated by

$$\begin{aligned}(\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D})_{p\mathbf{k}_p,q\mathbf{k}_q}=&[\mathbf{D}^\dagger(\mathbf{V}^\dagger\mathbf{h}\mathbf{V})^t\mathbf{D}]_{p\mathbf{k}_p,q\mathbf{k}_q}-\sum_{i\mathbf{k}_ij\mathbf{k}_j}(\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D})_{ji}g(p\mathbf{k}_pi\mathbf{k}_iq\mathbf{k}_qj\mathbf{k}_j)\\ &-\frac{1}{2}\sum_{j\mathbf{k}_jb\mathbf{k}_b}(\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D})^*_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pb\mathbf{k}_bq\mathbf{k}_qj\mathbf{k}_j)+\sum_{j\mathbf{k}_jb\mathbf{k}_b}(Q^t_{b\mathbf{k}_b,j\mathbf{k}_j})^*g(p\mathbf{k}_pb\mathbf{k}_bq\mathbf{k}_qj\mathbf{k}_j)\\ &-\frac{1}{2}\sum_{j\mathbf{k}_jb\mathbf{k}_b}(\mathbf{D}^\dagger\mathbf{s}_1^t\mathbf{D})_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pj\mathbf{k}_jq\mathbf{k}_qb\mathbf{k}_b)+\sum_{j\mathbf{k}_jb\mathbf{k}_b}Q^t_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pj\mathbf{k}_jq\mathbf{k}_qb\mathbf{k}_b)\\ &+\sum_{\mu\nu\lambda\sigma}(D^{\mathbf{k}_p}_{\mu p})^*D^{\mathbf{k}_q}_{\nu q}\sum_{\mathbf{k}}P^{\mathbf{k}}_{\lambda\sigma}\frac{\partial}{\partial y_t}[2\langle\bar{\phi}_{\mathbf{k}_p\mu}\bar{\phi}_{\mathbf{k}\lambda}|\bar{\phi}_{\mathbf{k}_q\nu}\bar{\phi}_{\mathbf{k}\sigma}\rangle-\langle\bar{\phi}_{\mathbf{k}_p\mu}\bar{\phi}_{\mathbf{k}\lambda}|\bar{\phi}_{\mathbf{k}\sigma}\bar{\phi}_{\mathbf{k}_q\nu}\rangle]\\ =&[\mathbf{C}^\dagger\mathbf{h}^t\mathbf{C}]_{p\mathbf{k}_p,q\mathbf{k}_q}-\sum_{i\mathbf{k}_ij\mathbf{k}_j}(\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C})_{ji}g(p\mathbf{k}_pi\mathbf{k}_iq\mathbf{k}_qj\mathbf{k}_j)\\ &-\frac{1}{2}\sum_{j\mathbf{k}_jb\mathbf{k}_b}(\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C})^*_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pb\mathbf{k}_bq\mathbf{k}_qj\mathbf{k}_j)+\sum_{j\mathbf{k}_jb\mathbf{k}_b}(Q^t_{b\mathbf{k}_b,j\mathbf{k}_j})^*g(p\mathbf{k}_pb\mathbf{k}_bq\mathbf{k}_qj\mathbf{k}_j)\\ &-\frac{1}{2}\sum_{j\mathbf{k}_jb\mathbf{k}_b}(\mathbf{C}^\dagger\mathbf{S}^t\mathbf{C})_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pj\mathbf{k}_jq\mathbf{k}_qb\mathbf{k}_b)+\sum_{j\mathbf{k}_jb\mathbf{k}_b}Q^t_{b\mathbf{k}_b,j\mathbf{k}_j}g(p\mathbf{k}_pj\mathbf{k}_jq\mathbf{k}_qb\mathbf{k}_b)\\ &+\sum_{\alpha\beta\gamma\theta}(C^{\mathbf{k}_p}_{\alpha p})^*C^{\mathbf{k}_q}_{\beta q}\sum_{\mathbf{k}}P^{\mathbf{k}}_{\gamma\theta}\frac{\partial}{\partial y_t}[2\langle\phi_{\mathbf{k}_p\alpha}\phi_{\mathbf{k}\gamma}|\phi_{\mathbf{k}_q\beta}\phi_{\mathbf{k}\theta}\rangle-\langle\phi_{\mathbf{k}_p\alpha}\phi_{\mathbf{k}\gamma}|\phi_{\mathbf{k}\theta}\phi_{\mathbf{k}_q\beta}\rangle]\\ &+[\mathbf{D}^\dagger(\mathbf{V}^t)^\dagger\mathbf{F}'\mathbf{C}+\mathbf{C}^\dagger\mathbf{F}'\mathbf{V}^t\mathbf{D}]_{p\mathbf{k}_p,q\mathbf{k}_q}+\sum_{j\mathbf{k}}\sum_{\beta\mathbf{k}_\beta}\sum_{\lambda}[(D^{\mathbf{k}}_{\lambda j})^*(V^t_{\mathbf{k}_\beta\beta,\mathbf{k}\lambda})^*\\ &\times g'(q\mathbf{k}_qj\mathbf{k}p\mathbf{k}_p\beta\mathbf{k}_\beta)^*+D^{\mathbf{k}}_{\lambda j}V^t_{\mathbf{k}_\beta\beta,\mathbf{k}\lambda}g'(p\mathbf{k}_pj\mathbf{k}q\mathbf{k}_q\beta\mathbf{k}_\beta)],\end{aligned} \tag{78}$$

where

$$g(p\mathbf{k}_p q\mathbf{k}_q r\mathbf{k}_r s\mathbf{k}_s) = 2\langle \psi_{p\mathbf{k}_p}\psi_{q\mathbf{k}_q}|\psi_{r\mathbf{k}_r}\psi_{s\mathbf{k}_s}\rangle - \langle \psi_{p\mathbf{k}_p}\psi_{q\mathbf{k}_q}|\psi_{s\mathbf{k}_s}\psi_{r\mathbf{k}_r}\rangle, \tag{79}$$

$$g'(p\mathbf{k}_p q\mathbf{k}_q r\mathbf{k}_r s\mathbf{k}_s) = 2\langle \psi_{p\mathbf{k}_p}\psi_{q\mathbf{k}_q}|\psi_{r\mathbf{k}_r}\phi_{s\mathbf{k}_s}\rangle - \langle \psi_{p\mathbf{k}_p}\psi_{q\mathbf{k}_q}|\phi_{s\mathbf{k}_s}\psi_{r\mathbf{k}_r}\rangle, \tag{80}$$

$$P^{\mathbf{k}}_{\lambda\sigma} = \sum_i^{\text{occ.}} (D^{\mathbf{k}}_{\lambda i})^* D^{\mathbf{k}}_{\sigma i}, \tag{81}$$

$$P^{\mathbf{k}}_{\gamma\theta} = \sum_i^{\text{occ.}} (C^{\mathbf{k}}_{\gamma i})^* C^{\mathbf{k}}_{\theta i}. \tag{82}$$

For the second derivatives, we can get

$$(\mathbf{U}^{tt'})^\dagger + \mathbf{U}^{tt'} = -\mathbf{D}^\dagger \mathbf{s}_1^{tt'}\mathbf{D} + (\mathbf{U}^{t'})^\dagger(\mathbf{U}^t)^\dagger + \mathbf{U}^t\mathbf{U}^{t'} - \mathbf{D}^\dagger\mathbf{s}_1^{t'}\mathbf{D}\mathbf{U}^t - (\mathbf{U}^t)^\dagger\mathbf{D}^\dagger\mathbf{s}_1^{t'}\mathbf{D}, \tag{83}$$

$$\boldsymbol{\epsilon}^{tt'} - (\mathbf{U}^{tt'})^\dagger\boldsymbol{\epsilon} - \boldsymbol{\epsilon}\mathbf{U}^{tt'} = \mathbf{D}^\dagger\mathbf{F}^{tt'}\mathbf{D} + \mathbf{D}^\dagger\mathbf{F}^t\mathbf{D}\mathbf{U}^{t'} + \mathbf{D}^\dagger\mathbf{F}^{t'}\mathbf{D}\mathbf{U}^t + (\mathbf{U}^t)^\dagger\mathbf{D}^\dagger\mathbf{F}^{t'}\mathbf{D} + (\mathbf{U}^{t'})^\dagger\mathbf{D}^\dagger\mathbf{F}^t\mathbf{D} + (\mathbf{U}^t)^\dagger\boldsymbol{\epsilon}\mathbf{U}^{t'} + (\mathbf{U}^{t'})^\dagger\boldsymbol{\epsilon}\mathbf{U}^t. \tag{84}$$

It is not difficult but tedious to give details for these equations. We do not go further here. In fact, one can use the formulas given in Ref. 17, provided the atomic orbitals are replaced by semisymmetrized functions defined in Sec. II.

IV. COUPLED-PERTURBED EQUATIONS WITH RESPECT TO SYMMETRIZED COORDINATES

Although the equations to get derivatives of the independent orbitals and their overlap matrix and the CPHF equations are given in Secs. II and III, respectively, the equations are very difficult to solve in practice, especially the CPHF equations, which are matrix equations with an infinite dimension. In this section, we will use symmetrized coordinates for nuclei to simplify the solutions, given in Eqs. (37)–(40), of coupled-perturbed equations for independent orbitals and also simplify the CPHF equations such that they can be easily solved.

A. Symmetrized coordinates

Let us define symmetrized coordinates as

$$Y = \{Y_1, \ldots, Y_t, \ldots\} = \{\ldots, Y_{\mathbf{k}A\tau}, \ldots\}$$

by

$$Y_{\mathbf{k}A\tau} = \frac{1}{\mathcal{N}}\sum_l e^{-i\mathbf{k}\cdot\mathbf{R}_l} y_{lA\tau} \tag{85}$$

or

$$\frac{\partial}{\partial Y_{\mathbf{k}A\tau}} = \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\frac{\partial}{\partial y_{lA\tau}}. \tag{86}$$

We can also express $y_{la\tau}$ or $\partial/\partial y_{lA\tau}$ in terms of the symmetrized coordinates, e.g.,

$$y_{lA\tau} = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_l} Y_{\mathbf{k}A\tau}, \tag{87}$$

$$\frac{\partial}{\partial y_{lA\tau}} = \frac{1}{\mathcal{N}}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_l}\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}. \tag{88}$$

From Eq. (87), we know that only when $\mathbf{k}=0$, the displacements of the corresponding nuclei in different units are the same. Therefore, all the coordinates with $\mathbf{k}=0$, $Y_{0A\tau}$, do not break the translational symmetry while others do. In the following, we will show that they behave like Bloch or symmetrized orbitals.

Now let us take the derivative of a semisymmetrized orbital $\phi_{\mathbf{k}_\alpha\alpha}(y,\mathbf{r})$ with respect to $Y_{\mathbf{k}A\tau}$ at $y=0$. From Eq. (86), we get

$$\left.\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\phi_{\mathbf{k}_\alpha\alpha}(y,\mathbf{r})\right|_{y=0} = \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\frac{\partial}{\partial y_{lA\tau}}\sum_{l'} e^{i\mathbf{k}_\alpha\cdot\mathbf{R}_{l'}}\chi_\alpha^{l'}(y,\mathbf{r})\bigg|_{y=0} = \sum_l e^{i(\mathbf{k}+\mathbf{k}_\alpha)\cdot\mathbf{R}_l}\frac{\partial}{\partial y_{lA\tau}}\chi_\alpha^l(y,\mathbf{r})\bigg|_{y=0}, \tag{89}$$

where use has been made of the fact that $\chi_\alpha^l(y,\mathbf{r})$ is not a function of $y_{l'A\tau}$ when $l'\neq l$. According to Eq. (24), we know that

$$\left.\frac{\partial}{\partial y_{lA\tau}}\chi_\alpha^l(y,\mathbf{r})\right|_{y=0} = \left.\frac{\partial}{\partial\Delta R_{lA\tau}}\chi_\alpha(\mathbf{r}-\mathbf{R}_l-\mathbf{R}_A-\Delta\mathbf{R}_{lA})\right|_{\Delta R_{lA\tau}=0} = \left.\frac{\partial}{\partial y_{0A\tau}}\chi_\alpha^0(y,\mathbf{r}-\mathbf{R}_l)\right|_{y=0}. \tag{90}$$

This indicates that

$$\hat{T}_{l'}\left.\frac{\partial}{\partial y_{lA\tau}}\chi_\alpha^l(y,\mathbf{r})\right|_{y=0} = \left.\frac{\partial}{\partial y_{(l-l')A\tau}}\chi_\alpha^{l-l'}(y,\mathbf{r})\right|_{y=0}, \tag{91}$$

where $\hat{T}_l$ is a translation operator which translates the position vector of the electron from $\mathbf{r}$ to be $\mathbf{r}+\mathbf{R}_l$. Then we have

$$\hat{T}_l\left.\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\phi_{\mathbf{k}_\alpha\alpha}(y,\mathbf{r})\right|_{y=0} = e^{(\mathbf{k}+\mathbf{k}_\alpha)\cdot\mathbf{R}_l}\left.\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\phi_{\mathbf{k}_\alpha\alpha}(y,\mathbf{r})\right|_{y=0}. \tag{92}$$

This means that $(\partial/\partial Y_{\mathbf{k}A\tau})\,\phi_{\mathbf{k}_\alpha\alpha}(y,\mathbf{r})|_{y=0}$ is a representation of the translational symmetry with a reciprocal vector $\mathbf{k}+\mathbf{k}_\alpha$, although the coordinate $Y_{\mathbf{k}A\tau}$ may break the translational symmetry. Similarly, for an operator $\hat{O}$ having translational symmetry when $y=0$, one can show that $\partial\hat{O}(y)/\partial Y_{\mathbf{k}A\tau}|_{y=0}$ is also a representation of the translational symmetry with a reciprocal lattice $\mathbf{k}$. Then for a translation operator T_l which translates the system by $\mathbf{R}_l$, we have

$$\hat{T}_l\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}(\langle\phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi'_{\mathbf{k}_\beta\beta}\rangle) = e^{i(\mathbf{k}+\mathbf{k}_\beta-\mathbf{k}_\alpha)\cdot\mathbf{R}_l}\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}(\langle\phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi_{\mathbf{k}_\beta\beta}\rangle), \tag{93}$$

where the subscription $y=0$ is omitted. Since we are only interested in derivatives at $y=0$, we will omit the subscript in the following. Equation (93) implies that

$$\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}(\langle \phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi_{\mathbf{k}_\beta\beta}\rangle)$$
$$=\delta_{\mathbf{k}\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}_\beta)}\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}(\langle \phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi_{\mathbf{k}_\beta\beta}\rangle), \tag{94}$$

where $\mathbf{T}(x)$ is an operator which takes x back to the reciprocal lattice space defined in Sec. II A whenever it is out of the region.[26] Equation (94) tells us that an element of the matrix fails to vanish only when the difference of the orbitals reciprocal lattices matches the symmetry of the symmetrized orbital.

Similarly, we also get

$$\frac{\partial^2}{\partial Y_{\mathbf{k}A\tau}\partial Y_{\mathbf{k}'A'\tau'}}(\langle \phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi_{\mathbf{k}_\beta\beta}\rangle)$$
$$=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}'+\mathbf{k}_\beta)}\frac{\partial^2}{\partial Y_{\mathbf{k}A\tau}\partial Y_{\mathbf{k}'A'\tau'}}(\langle \phi_{\mathbf{k}_\alpha\alpha}|\hat{O}|\phi_{\mathbf{k}_\beta\beta}\rangle) \tag{95}$$

for second derivatives.

B. Derivatives of independent orbitals and their overlap matrix

According to Eqs. (25), (86), and (94), the first derivatives of the overlap matrix over semisymmetric orbitals with respect to $Y_{\mathbf{k}A\tau}$ can be evaluated by

$$S^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}S_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}$$
$$=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}_\beta)}\sum_l\left[e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}\left\langle\frac{\partial}{\partial y_{0A\tau}}\chi^0_\alpha\middle|\chi^l_\beta\right\rangle+e^{-i\mathbf{k}_\alpha\cdot\mathbf{R}_l}\left\langle\chi^l_\alpha\middle|\frac{\partial}{\partial y_{0A\tau}}\chi^0_\beta\right\rangle\right]. \tag{96}$$

Then Eqs. (37) and (38) can be rewritten as

$$s^{\mathbf{k}A\tau}_{\mathbf{k}'\mu,\mathbf{k}''\mu'}=\delta_{\mathbf{k}',\mathbf{T}(\mathbf{k}+\mathbf{k}'')}\sum_{\alpha\beta}(V^{\mathbf{k}'}_{\alpha\mu})^*S^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}V^{\mathbf{T}(\mathbf{k}'-\mathbf{k})}_{\beta\mu'},$$
$$\mu,\mu'\leqslant M\quad or\quad \mu,\mu'>M, \tag{97}$$

$$A^{\mathbf{k}A\tau}_{\mathbf{k}'\mu,\mathbf{k}''\mu'}=\frac{\delta_{\mathbf{k}',\mathbf{T}(\mathbf{k}+\mathbf{k}'')}}{\lambda_{\mathbf{T}(\mathbf{k}'-\mathbf{k})\mu'}-\lambda_{\mathbf{k}'\mu}}\sum_{\alpha\beta}(V^{\mathbf{k}'}_{\alpha\mu})^*\times S^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}V^{\mathbf{T}(\mathbf{k}'-\mathbf{k})}_{\beta\mu'},\quad \mu\leqslant M;\mu'>M. \tag{98}$$

Then there are no infinite summations any more in the expressions for first derivatives of the independent orbitals and their overlap matrix and only the blocks which satisfy the condition that

$$\mathbf{k}'=\mathbf{k}''+\mathbf{k} \tag{99}$$

have nonzero values.

The second derivatives of the overlap matrix with respect to $Y_{\mathbf{k}A\tau}$ and $Y_{\mathbf{k}'A'\tau'}$ are given by

$$S^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\frac{\partial^2 S_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}$$
$$=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}_\beta+\mathbf{k}+\mathbf{k}')}\sum_l\left[e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}\left\langle\frac{\partial^2\chi^0_\alpha}{\partial y^2_{0A\tau}}\middle|\chi^l_\beta\right\rangle+e^{-i\mathbf{k}_\alpha\cdot\mathbf{R}_l}\left\langle\chi^l_\alpha\middle|\frac{\partial^2\chi^0_\beta}{\partial y^2_{0A\tau}}\right\rangle+e^{i(\mathbf{k}'+\mathbf{k}_\beta)\cdot\mathbf{R}_l}\left\langle\frac{\partial\chi^0_\alpha}{\partial y_{0A\tau}}\middle|\frac{\partial\chi^l_\beta}{\partial y_{lA'\tau'}}\right\rangle+e^{i(\mathbf{k}+\mathbf{k}_\beta)\cdot\mathbf{R}_l}\left\langle\frac{\partial\chi^0_\alpha}{\partial y_{0A'\tau'}}\middle|\frac{\partial\chi^l_\beta}{\partial y_{lA\tau}}\right\rangle\right]. \tag{100}$$

Substituting Eqs. (97), (98), and (100) into Eqs. (39) and (40), we can get

$$\begin{aligned}s^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{k}_{\mu'}\mu'}=\delta_{\mathbf{k}_\mu,\mathbf{T}(\mathbf{k}_{\mu'}+\mathbf{k}+\mathbf{k}')}\Bigg[&\sum_{\alpha,\beta=1}^{T}(V^{\mathbf{k}_\mu}_{\alpha\mu})^*S^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\alpha,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\beta}V^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')}_{\alpha\mu'}\\&-\frac{1}{2}\sum_{\mu_1=M+1}^{T}\sum_{\mu_2=1}^{M}\Big(A^{\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1}A^{\mathbf{k}A\tau}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu_2}\\&+A^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1}A^{\mathbf{k}'A'\tau'}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu_2}\Big)s^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')}_{\mu_2\mu'}\\&-\frac{1}{2}\sum_{\mu_1=1}^{M}\sum_{\mu_2=M+1}^{T}s^{\mathbf{k}_\mu}_{\mu\mu_1}(A^{\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_2}A^{\mathbf{k}A\tau}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_2,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}+A^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_2}A^{\mathbf{k}'A'\tau'}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_2,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'})\\&+\sum_{\mu_1=M+1}^{T}\sum_{\mu_2=M+1}^{T}A^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1}s^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})}_{\mu_1\mu_2}A^{\mathbf{k}'A'\tau'}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_2,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}\\&+\sum_{\mu_1=M+1}^{T}\sum_{\mu_2=M+1}^{T}A^{\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1}s^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')}_{\mu_1\mu_2}\mathbf{A}^{\mathbf{k}A\tau}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_2,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}\Bigg],\quad \mu,\mu'\leqslant M,\end{aligned} \tag{101}$$

$$A^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{k}_{\mu'}\mu'}=\frac{\delta_{\mathbf{k}_\mu,\mathbf{T}(\mathbf{k}_{\mu'}+\mathbf{k}+\mathbf{k}')}}{\lambda_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}-\lambda_{\mathbf{k}_\mu\mu}}\Bigg[\sum_{\alpha,\beta=1}^{T}(V^{\mathbf{k}_\mu}_{\alpha\mu})^*S^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\alpha,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\beta}V^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')}_{\alpha\mu'}$$
$$-\sum_{\mu_1=M+1}^{T}A^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1}s^{\mathbf{k}'A'\tau'}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}-\sum_{\mu_1=M+1}^{T}A^{\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1}s^{\mathbf{k}A\tau}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}$$
$$+\sum_{\mu_1=1}^{M}s^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1}A^{\mathbf{k}'A'\tau'}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}$$
$$+\sum_{\mu_1=1}^{M}s^{\mathbf{k}'A'\tau'}_{\mathbf{k}_\mu\mu,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1}A^{\mathbf{k}A\tau}_{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}')\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k}-\mathbf{k}')\mu'}\Bigg],\quad \mu\leqslant M;\mu'>M. \tag{102}$$

As for first derivatives, there are no infinite summations in Eqs. (101) and (102).

Since overlap matrices are Hermitian, we can conclude that

$$(\mathbf{S}^{\mathbf{k}A\tau\cdots})^\dagger=\mathbf{S}^{-\mathbf{k}A\tau\cdots}, \tag{103}$$

$$(\mathbf{s}^{\mathbf{k}A\tau\cdots})^\dagger=\mathbf{s}^{-\mathbf{k}A\tau\cdots}, \tag{104}$$

which are valid for any order. From Eqs. (98) and (102), we can get

$$(\mathbf{A}^{\mathbf{k}A\tau})^\dagger=-\mathbf{A}^{-\mathbf{k}A\tau}, \tag{105}$$

$$(\mathbf{A}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}_{12})^\dagger=-\mathbf{A}^{-\mathbf{k}A\tau-\mathbf{k}'A'\tau'}_{21}. \tag{106}$$

From Eq. (25), we also know that

$$(S^{\mathbf{k}A\tau\cdots}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta})^*=S^{-\mathbf{k}A\tau\cdots}_{-\mathbf{k}_\alpha\alpha,-\mathbf{k}_\beta\beta}. \tag{107}$$

Then from Eqs. (106) and (107), we can obtain that

$$(\mathbf{A}^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{k}_{\mu'}\mu'})^*=\mathbf{A}^{-\mathbf{k}A\tau}_{-\mathbf{k}_\mu\mu,-\mathbf{k}_{\mu'}\mu'}. \tag{108}$$

The above relationships can be directly checked from Eqs. (96)–(98) and (100)–(102).

C. Derivatives of the HF orbitals and the orbital energy matrix

From Eqs. (73) and (86), we obtain

$$P^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu,\mathbf{k}_{\mu'}\mu'}=-\frac{\delta_{\mathbf{k}_\mu,\mathbf{T}(\mathbf{k}_{\mu'}+\mathbf{k})}}{2}\sum_{\mu_1\mu_2}(D^{\mathbf{k}_\mu}_{\mu_1\mu})^*\times s^{\mathbf{k}A\tau}_{\mathbf{k}_\mu\mu_1,\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})\mu_2}D^{\mathbf{T}(\mathbf{k}_\mu-\mathbf{k})}_{\mu_2\mu'}. \tag{109}$$

Then it is not difficult to calculate $\mathbf{P}^{\mathbf{k}A\tau}$. It is easy to see that

$$(\mathbf{P}^{\mathbf{k}A\tau})^\dagger=\mathbf{P}^{-\mathbf{k}A\tau}. \tag{110}$$

Either directly from Eqs. (70) and (71) or Eqs. (76) and (77), we can also get

$$(\mathbf{Q}^{\mathbf{k}A\tau})^\dagger=-\mathbf{Q}^{-\mathbf{k}A\tau}, \tag{111}$$

$$(\boldsymbol{\epsilon}^{\mathbf{k}A\tau})^\dagger=\boldsymbol{\epsilon}^{-\mathbf{k}A\tau}. \tag{112}$$

In order to write formulas in a compact form, let us introduce the following notations,

$$\hat{h}^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\mathbf{k}_\alpha\alpha}|\hat{h}|\phi_{\mathbf{k}_\beta\beta}\rangle, \tag{113}$$

$$J^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\sum_{\gamma\theta}\sum_{\mathbf{k}}P^{\mathbf{k}}_{\gamma\theta}\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\mathbf{k}_\alpha\alpha}\phi_{\mathbf{k}\gamma}|\phi_{\mathbf{k}_\beta\beta}\phi_{\mathbf{k}\theta}\rangle, \tag{114}$$

$$K^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\sum_{\gamma\theta}\sum_{\mathbf{k}}P^{\mathbf{k}}_{\gamma\theta}\frac{\partial}{\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\mathbf{k}_\alpha\alpha}\phi_{\mathbf{k}\gamma}|\phi_{\mathbf{k}\theta}\phi_{\mathbf{k}_\beta\beta}\rangle. \tag{115}$$

According to Eqs. (23), (65), (82), and (86), we have

$$\hat{h}^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}_\beta)}\sum_l\Bigg[e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}\left\langle\frac{\partial}{\partial y_{0A\tau}}\chi^0_\alpha|\hat{h}|\chi^l_\beta\right\rangle+e^{-i\mathbf{k}_\alpha\cdot\mathbf{R}_l}\langle\chi^l_\alpha|\hat{h}|\frac{\partial}{\partial y_{0A\tau}}\chi^0_\beta\rangle+e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}\sum_{l'}e^{i\mathbf{k}\cdot\mathbf{R}_{l'}}\langle\chi^0_\alpha|\frac{\partial}{\partial y_{l'A\tau}}\hat{h}(l')|\chi^l_\beta\rangle\Bigg], \tag{116}$$

$$J^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}_\beta)}\sum_l\sum_{hh'}\sum_{\gamma\theta}\times\Bigg[e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}D^{hh'}_{\gamma\theta}\left(\frac{\partial\chi^0_\alpha}{\partial y_{0A\tau}}\chi^l_\beta\middle|\chi^h_\gamma\chi^{h'}_\theta\right)+e^{-i\mathbf{k}_\alpha\cdot\mathbf{R}_l}D^{hh'}_{\gamma\theta}\left(\chi^l_\alpha\frac{\partial\chi^0_\beta}{\partial y_{0A\tau}}\middle|\chi^h_\gamma\chi^{h'}_\theta\right)+e^{i(\mathbf{k}_\beta\cdot\mathbf{R}_l-\mathbf{k}_\alpha\cdot\mathbf{R}_{h'})}D^{0h}_{\gamma\theta}\left(\chi^{h'}_\alpha\chi^l_\beta\middle|\frac{\partial\chi^0_\gamma}{\partial y_{0A\tau}}\chi^h_\theta\right)+e^{i(\mathbf{k}_\beta\cdot\mathbf{R}_l-\mathbf{k}_\alpha\cdot\mathbf{R}_{h'})}D^{h0}_{\gamma\theta}\left(\chi^{h'}_\alpha\chi^l_\beta\middle|\chi^h_\gamma\frac{\partial\chi^0_\theta}{\partial y_{0A\tau}}\right)\Bigg], \tag{117}$$

$$K^{\mathbf{k}A\tau}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}=\delta_{\mathbf{k}_\alpha,\mathbf{T}(\mathbf{k}+\mathbf{k}_\beta)}\sum_l\sum_{hh'}\sum_{\gamma\theta}\left[e^{i\mathbf{k}_\beta\cdot\mathbf{R}_l}D^{hh'}_{\gamma\theta}\left(\frac{\partial\chi^0_\alpha}{\partial y_{0A\tau}}\chi^{h'}_\theta\middle|\chi^h_\gamma\chi^l_\beta\right)+e^{-i\mathbf{k}_\alpha\cdot\mathbf{R}_l}D^{hh'}_{\gamma\theta}\left(\chi^l_\alpha\chi^{h'}_\theta\middle|\chi^h_\gamma\frac{\partial\chi^0_\beta}{\partial y_{0A\tau}}\right)+e^{i(\mathbf{k}_\beta\cdot\mathbf{R}_l-\mathbf{k}_\alpha\cdot\mathbf{R}_{h'})}D^{h0}_{\gamma\theta}\right.$$
$$\left.\times\left(\chi^{h'}_\alpha\frac{\partial\chi^0_\theta}{\partial y_{0A\tau}}\middle|\chi^h_\gamma\chi^l_\beta\right)+e^{i(\mathbf{k}_\beta\cdot\mathbf{R}_l-\mathbf{k}_\alpha\cdot\mathbf{R}_h)}D^{0h}_{\gamma\theta}\left(\chi^h_\alpha\chi^{h'}_\theta\middle|\frac{\partial\chi^0_\gamma}{\partial y_{0A\tau}}\chi^l_\beta\right)\right].\qquad(118)$$

Substituting Eqs. (113), (114), and (115) into Eq. (78) and then substituting Eq. (78) into Eq. (77), we get

$$(\epsilon_{i\mathbf{k}_i}-\epsilon_{a\mathbf{k}_a})Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}=B^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}+\frac{1}{\mathcal{W}}\sum_{jb}\int d\mathbf{k}_b[(Q^{-\mathbf{k}A\tau}_{b\mathbf{k}_b,j\mathbf{T}(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)})^*G(a\mathbf{k}_ab\mathbf{k}_bi\mathbf{k}_ij\mathbf{T}(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i))$$
$$+Q^{\mathbf{k}A\tau}_{b\mathbf{k}_b,j\mathbf{T}(\mathbf{k}_b+\mathbf{k}_i-\mathbf{k}_a)}G(a\mathbf{k}_aj\mathbf{T}(\mathbf{k}_b+\mathbf{k}_i-\mathbf{k}_a)i\mathbf{k}_ib\mathbf{k}_b)],\qquad(119)$$

where

$$B^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}=\delta_{\mathbf{k}_a,\mathbf{k}_i+\mathbf{k}}\left\{\sum_{\alpha\beta}(C^{\mathbf{k}_a}_{\alpha,a})^*h^{\mathbf{k}A\tau}_{\mathbf{k}_a\alpha,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta}C^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta,i}+\sum_{\alpha\beta\gamma\theta}(C^{\mathbf{k}_a}_{\alpha a})^*[2J^{\mathbf{k}A\tau}_{\mathbf{k}_a\alpha,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta}-K^{\mathbf{k}A\tau}_{\mathbf{k}_a\alpha,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta}]C^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta,i}\right.$$
$$-\frac{1}{\mathcal{W}}\sum_{i'j'}\sum_{\alpha\beta}\int d\mathbf{k}_{j'}(C^{\mathbf{k}_{j'}}_{\alpha,j'})^*S^{\mathbf{T}A\tau}_{\mathbf{k}_{j'}\alpha,\mathbf{T}(\mathbf{k}_{j'}-\mathbf{k})\beta}C^{\mathbf{T}(\mathbf{k}_{j'}-\mathbf{k})}_{\beta,i'}G(a\mathbf{k}_ai'\mathbf{T}(\mathbf{k}_{j'}-\mathbf{k})i\mathbf{T}(\mathbf{k}_a-\mathbf{k})j'\mathbf{k}_{j'})$$
$$-\frac{1}{2}[(C^{\mathbf{k}_a}_{\alpha,a})^*S^{\mathbf{k}A\tau}_{\mathbf{k}_a\alpha,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta}C^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta,i}\epsilon_{i\mathbf{T}(\mathbf{k}_a-\mathbf{k})}+\epsilon_{a\mathbf{k}_a}(C^{\mathbf{k}_a}_{\alpha,a})^*S^{\mathbf{k}A\tau}_{\mathbf{k}_a\alpha,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta}C^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta,i}]$$
$$-\frac{1}{2\mathcal{W}}\sum_{bj}\sum_{\alpha\beta}\int d\mathbf{k}_bC^{\mathbf{k}_b}_{\alpha,b}S^{\mathbf{k}A\tau}_{-\mathbf{k}_b\alpha,-\mathbf{T}(\mathbf{k}_b+\mathbf{k})\beta}(C^{\mathbf{T}(\mathbf{k}_b+\mathbf{k})}_{\beta,j})^*G(a\mathbf{k}_ab\mathbf{k}_bi\mathbf{T}(\mathbf{k}_a-\mathbf{k})j\mathbf{T}(\mathbf{k}_b+\mathbf{k}))$$
$$-\frac{1}{2\mathcal{W}}\sum_{bj}\sum_{\alpha\beta}\int d\mathbf{k}_b(C^{\mathbf{k}_b}_{\alpha,b})^*S^{\mathbf{k}A\tau}_{\mathbf{k}_b\alpha,\mathbf{T}(\mathbf{k}_b-\mathbf{k})\beta}C^{\mathbf{T}(\mathbf{k}_b-\mathbf{k})}_{\beta,j}G(a\mathbf{k}_aj\mathbf{T}(\mathbf{k}_b-\mathbf{k})i\mathbf{T}(\mathbf{k}_a-\mathbf{k})b\mathbf{k}_b)$$
$$+\sum_{\mu\alpha\beta}[(D^{\mathbf{k}_a}_{\mu a})^*(V^{-\mathbf{k}A\tau}_{\alpha\mathbf{T}(\mathbf{k}_a-\mathbf{k}),\mu\mathbf{k}_a})^*F'^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\alpha\beta}C^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta i}+(C^{\mathbf{k}_a}_{\alpha a})^*F'^{\mathbf{k}_a}_{\alpha\beta}\mathbf{V}^{\mathbf{k}A\tau}_{\mathbf{k}_a\beta,\mathbf{T}(\mathbf{k}_a-\mathbf{k})\mu}D^{\mathbf{T}(\mathbf{k}_a-\mathbf{k})}_{\beta i}]$$
$$+\sum_{i\beta\lambda}\frac{1}{\mathcal{W}}\int d\mathbf{k}_\beta[(D^{\mathbf{T}(\mathbf{k}_\beta+\mathbf{k})}_{\lambda j})^*(V^{-\mathbf{k}A\tau}_{\beta\mathbf{k}_\beta,\lambda\mathbf{T}(\mathbf{k}_\beta+\mathbf{k})})^*G'(i\mathbf{T}(\mathbf{k}_a-\mathbf{k})j\mathbf{T}(\mathbf{k}_\beta+\mathbf{k})a\mathbf{k}_a\beta\mathbf{k}_\beta)^*$$
$$\left.+D^{\mathbf{T}(\mathbf{k}_\beta-\mathbf{k})}_{\lambda j}V^{\mathbf{k}A\tau}_{\mathbf{k}_\beta\beta,\mathbf{T}(\mathbf{k}_\beta-\mathbf{k})\lambda}G'(a\mathbf{k}_aj\mathbf{T}(\mathbf{k}_\beta-\mathbf{k})i\mathbf{T}(\mathbf{k}_a-\mathbf{k})\beta\mathbf{k}_\beta)\right].\qquad(120)$$

The functions G and G' used in Eqs. (119) and (120) are defined as

$$G(p\mathbf{k}_pq\mathbf{k}_qr\mathbf{k}_rs\mathbf{k}_s)=2Q(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)-Q(pqsr\mathbf{k}_p\mathbf{k}_s\mathbf{k}_r),\qquad(121)$$

$$G'(p\mathbf{k}_pq\mathbf{k}_qr\mathbf{k}_rs\mathbf{k}_s)=2Q'(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)-Q'(pqsr\mathbf{k}_p\mathbf{k}_s\mathbf{k}_r),\qquad(122)$$

where $Q(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$ was defined in Eq. (37) of Ref. 26 and $Q'(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$ can be obtained by replacing $\psi_{s\mathbf{k}_s}$ with $\phi_{s\mathbf{k}_s}$ in the expression of the former. It is easy to see that each term in Eq. (120) has a finite value and so does $B^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$.

Since $\mathbf{T}(\mathbf{T}(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)-\mathbf{k}_b)=\mathbf{T}(\mathbf{k}_a-\mathbf{k}_i)$, any two $Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ are not coupled by Eq. (119) if the differences of their reciprocal lattices are different. In other words, we can classify $Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ into groups according to $\mathbf{T}(\mathbf{k}_a-\mathbf{k}_i)$. In each group, $\mathbf{T}(\mathbf{k}_a-\mathbf{k}_i)$ is a constant. For a group with $\mathbf{T}(\mathbf{k}_a-\mathbf{k}_i)\neq 0$, all concerned $B^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ are zero according to Eqs. (120). Since Eq. (119) are linear equations of the quantities, we can conclude that all $Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ in the group are zero and then we can conclude all $Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ are zero except those that satisfy $\mathbf{T}(\mathbf{k}_a-\mathbf{k}_i)=0$. Then we can write

$$Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}=\delta_{\mathbf{k}_a,\mathbf{T}(\mathbf{k}_i+\mathbf{k})}Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,iT(\mathbf{k}_a-\mathbf{k})}.\qquad(123)$$

Then the CPHF equations can be rewritten as

$$(\epsilon_{iT(\mathbf{k}'-\mathbf{k})}-\epsilon_{a\mathbf{k}'})Q^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})}=B^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})}+\frac{1}{\mathcal{W}}\sum_{jb}\int d\mathbf{k}''[G(a\mathbf{k}'b(-\mathbf{k}'')\times i\mathbf{T}(\mathbf{k}'-\mathbf{k})j\mathbf{T}(-\mathbf{k}''+\mathbf{k}))(Q^{-\mathbf{k}A\tau}_{b(-\mathbf{k}''),j\mathbf{T}(-\mathbf{k}''+\mathbf{k})})^*+G(a\mathbf{k}'j\mathbf{T}(\mathbf{k}''-\mathbf{k})i\mathbf{T}(\mathbf{k}'-\mathbf{k})b\mathbf{k}'')Q^{\mathbf{k}A\tau}_{b\mathbf{k}'',j\mathbf{T}(\mathbf{k}''-\mathbf{k})}].\qquad(124)$$

Taking the complex conjugate of Eq. (120) and substituting Eqs. (11), (13), (58), (59), (103)–(108), (111), and (112) into the right side of the equation, we can obtain

$$(B^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i})^* = B^{-\mathbf{k}A\tau}_{a(-\mathbf{k}_a),i(-\mathbf{k}_i)}. \tag{125}$$

Then from Eqs. (124) and (125), we can get

$$\begin{aligned}(\epsilon_{iT(\mathbf{k}'-\mathbf{k})}-\epsilon_{a\mathbf{k}'})(Q^{-\mathbf{k}A\tau}_{a(-\mathbf{k}'),i\mathbf{T}(-\mathbf{k}'+\mathbf{k})})^* &= B^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})} + \frac{1}{\mathcal{W}}\sum_{jb}\int d\mathbf{k}''[G(a\mathbf{k}'b(-\mathbf{k}'')\\ &\quad\times i\mathbf{T}(\mathbf{k}'-\mathbf{k})j\mathbf{T}(-\mathbf{k}''+\mathbf{k}))Q^{\mathbf{k}A\tau}_{b\mathbf{k}'',j\mathbf{T}(\mathbf{k}''-\mathbf{k})}\\ &\quad+G(a\mathbf{k}'j\mathbf{T}(\mathbf{k}''-\mathbf{k})i\mathbf{T}(\mathbf{k}'-\mathbf{k})b\mathbf{k}'')\\ &\quad\times(Q^{-\mathbf{k}A\tau}_{b(-\mathbf{k}''),j\mathbf{T}(-\mathbf{k}''+\mathbf{k})})^*].\end{aligned} \tag{126}$$

Equations (124) and (126) tell us that

$$\left(Q^{-\mathbf{k}A\tau}_{b(-\mathbf{k}''),j\mathbf{T}(-\mathbf{k}''+\mathbf{k})}\right)^* = Q^{\mathbf{k}A\tau}_{b\mathbf{k}'',j\mathbf{T}(\mathbf{k}''-\mathbf{k})}. \tag{127}$$

Then substituting Eq. (127) into (124), we get

$$\begin{aligned}(\epsilon_{iT(\mathbf{k}'-\mathbf{k})}-\epsilon_{a\mathbf{k}'})Q^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})} &= B^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})} + \frac{1}{\mathcal{W}}\sum_{jb}\int d\mathbf{k}''[G(a\mathbf{k}'b(-\mathbf{k}'')\\ &\quad\times i\mathbf{T}(\mathbf{k}'-\mathbf{k})j\mathbf{T}(-\mathbf{k}''+\mathbf{k}))+G(a\mathbf{k}'j\mathbf{T}(\mathbf{k}''-\mathbf{k})\\ &\quad\times i\mathbf{T}(\mathbf{k}'-\mathbf{k})b\mathbf{k}'')]Q^{\mathbf{k}A\tau}_{b\mathbf{k}'',j\mathbf{T}(\mathbf{k}''-\mathbf{k})}.\end{aligned} \tag{128}$$

Equation (128) is a set of linear equations for $Q^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{k}'-\mathbf{k}}$. It is important to notice that they do not become more difficult to solve when $\mathbf{k}\neq 0$. This means that the amount of calculation needed for the derivative with respect to a displacement which breaks translational symmetry is about the same as that needed for the derivative with respect to a displacement which keeps the translational symmetry.

In real calculations, we do not need to determine all the nonzero $Q^{\mathbf{k}A\tau}_{a\mathbf{k}',iT(\mathbf{k}'-\mathbf{k})}$ since they are supposed to be smooth functions of $\mathbf{k}'$. We can take a finite number of points in the reciprocal lattice space, say $\{\mathbf{k}_m, m=1,\ldots,K\}$, and then we can transform Eq. (128) to be linear equations for $Q^{\mathbf{k}A\tau}_{a\mathbf{k}',iT(\mathbf{k}'-\mathbf{k})}$ at the points. To be efficient, one may need to take the so called ''special'' sets of $\mathbf{k}$-points in the irreducible segment of the Brillouin zone[19,29,30] as the set of points to solve Eq. (128). But for convenience, we just let the K-points be evenly distributed in the region in our following discussion. Let us define

$$\begin{aligned}G^{\mathbf{k}}_{ia\mathbf{k}_m,jb\mathbf{k}_{m'}} &= (\epsilon_{i\mathbf{T}(\mathbf{k}_m-\mathbf{k})}-\epsilon_{a\mathbf{k}_m})\delta_{ij}\delta_{ab}\delta_{mm'}\\ &\quad-\frac{1}{K}[G(a\mathbf{k}_m b(-\mathbf{k}_{m'})i\mathbf{T}(\mathbf{k}_m-\mathbf{k})\\ &\quad\times j\mathbf{T}(-\mathbf{k}_{m'}+\mathbf{k}))+G(a\mathbf{k}_m j\mathbf{T}(\mathbf{k}_{m'}-\mathbf{k})\\ &\quad\times i\mathbf{T}(\mathbf{k}_m-\mathbf{k})b\mathbf{k}_{m'})].\end{aligned} \tag{129}$$

Then the solution of Eq. (129) is given by[17,31]

$$\mathbf{Q}^{\mathbf{k}A\tau} = (\mathbf{G}^{\mathbf{k}})^{-1}\mathbf{B}^{\mathbf{k}A\tau}. \tag{130}$$

When $\mathbf{k}=0$, one must be careful to use Eq. (130) since $G^{\mathbf{k}}_{ia\mathbf{k}_m,jb\mathbf{k}_{m'}}$ may diverge when $\mathbf{k}_m=\mathbf{k}_{m'}$. In this case one may solve Eq. (128) iteratively.

Another way to solve Eq. (128) is to express $Q^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})}$ as its Fourier expansion over $\mathbf{k}'$ in the first Brillouin zone and then Eq. (128) becomes the linear equations of the Fourier coefficients. With these coefficients, one can calculate $Q^{\mathbf{k}A\tau}_{a\mathbf{k}',i\mathbf{T}(\mathbf{k}'-\mathbf{k})}$ at any given $\mathbf{k}'$.

After $Q^{\mathbf{k}A\tau}_{a\mathbf{k}_a,i\mathbf{k}_i}$ are determined, the first derivatives of the eigenvalue matrix can be calculated by

$$\epsilon^{\mathbf{k}A\tau}_{p\mathbf{k}_p,q\mathbf{k}_q} = \delta_{\mathbf{k}_p,\mathbf{k}_q+\mathbf{k}}\epsilon^{\mathbf{k}A\tau}_{p\mathbf{k}_p,q\mathbf{T}(\mathbf{k}_p-\mathbf{k})}, \tag{131}$$

where

$$\begin{aligned}\epsilon^{\mathbf{k}A\tau}_{p\mathbf{k}',q\mathbf{T}(\mathbf{k}'-\mathbf{k})} &= [\mathbf{D}^\dagger\mathbf{F}^{\mathbf{k}A\tau}\mathbf{D}-\tfrac{1}{2}(\mathbf{C}^\dagger\mathbf{S}^{\mathbf{k}A\tau}\mathbf{C}\boldsymbol{\epsilon}\\ &\quad+\boldsymbol{\epsilon}\mathbf{C}^\dagger\mathbf{S}^{\mathbf{k}A\tau}\mathbf{C})]_{p\mathbf{k}',q\mathbf{T}(\mathbf{k}'-\mathbf{k})},\\ &\quad p,q\leq n \quad or \quad p,q>n.\end{aligned} \tag{132}$$

With the same procedure, one can get explicit equations for second derivatives of the coefficients and eigenvalue matrix with respect to symmetrized coordinates.

V. ANALYTICAL DERIVATIVES OF THE HARTREE-FOCK ENERGY

A. Gradients

Differentiating both sides of Eq. (51) with respect to $Y_{\mathbf{k}A\tau}$, we get

$$\begin{aligned}\frac{\partial E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A\tau}} &= 2\sum_{\mathbf{k}'}\sum_{\alpha\beta}P^{\mathbf{k}'}_{\alpha\beta}h^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{k}'\beta}\\ &\quad+\sum_{\mathbf{k}'}\sum_{\alpha\beta}P^{\mathbf{k}'}_{\alpha\beta}[2J^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{k}'\beta}-K^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{k}'\beta}]\\ &\quad+2\sum_{i\mathbf{k}'}[\mathbf{D}^\dagger(\mathbf{V}^{-\mathbf{k}A\tau})^\dagger\mathbf{F}'\mathbf{C}+\mathbf{C}^\dagger\mathbf{F}'\mathbf{V}^{\mathbf{k}A\tau}\mathbf{D}]_{i\mathbf{k}',i\mathbf{k}'}\\ &\quad-2\sum_{\mathbf{k}'}\sum_{\alpha\beta}W^{\mathbf{k}'}_{\alpha\beta}S^{\mathbf{k}A\tau}_{\mathbf{k}'\alpha,\mathbf{k}'\beta}+\frac{\partial V_{\mathrm{nuc}}}{\partial Y_{\mathbf{k}A\tau}},\end{aligned} \tag{133}$$

where $W^{\mathbf{k}}_{\alpha\beta}$ is the ''energy-weighted density matrix'' defined as

$$W^{\mathbf{k}}_{\alpha\beta} = \sum_i^{\mathrm{occ.}}\epsilon_{i\mathbf{k}}(C^{\mathbf{k}}_{\alpha i})^* C^{\mathbf{k}}_{\beta i}. \tag{134}$$

From Eq. (94), we know that

$$\frac{\partial E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A\tau}} = \delta_{\mathbf{k},0}\frac{\partial E^{\mathrm{HF}}}{\partial Y_{\mathbf{0}A\tau}}. \tag{135}$$

This means that the gradient only has nonzero projections onto symmetrized coordinates when $\mathbf{k}=0$. When $\mathbf{k}=0$, we get

$$y_{lA\tau}=Y_{\mathbf{k}A\tau},\quad l=0,\mp 1,\mp 2,\ldots \tag{136}$$

from Eq. (86), e.g., the system keeps the periodicity when it changes its geometry along the coordinate. In this case, let us use $y_{A\tau}$ to denote the common displacement in the direction τ of all the nuclei described by A. Then we have

$$\frac{\partial E_{uc}^{\mathrm{HF}}}{\partial Y_{\mathbf{0}A\tau}}=\frac{\partial E_{uc}^{\mathrm{HF}}}{\partial y_{A\tau}}=\frac{1}{\mathcal{N}}\frac{\partial E^{\mathrm{HF}}}{\partial Y_{\mathbf{0}A\tau}}=\frac{1}{\mathcal{W}}\int\sum_{\alpha\beta}P_{\alpha\beta}^{\mathbf{k}}[2h_{\mathbf{k}\alpha,\mathbf{k}\beta}^{\mathbf{0}A\tau}+2J_{\mathbf{k}\alpha,\mathbf{k}\beta}^{\mathbf{0}A\tau}-K_{\mathbf{k}\alpha,\mathbf{k}\beta}^{\mathbf{0}A\tau}]d\mathbf{k}-\frac{2}{\mathcal{W}}\int\sum_{\alpha\beta}W_{\alpha\beta}^{\mathbf{k}}S_{\mathbf{k}\alpha,\mathbf{k}\beta}^{\mathbf{0}A\tau}d\mathbf{k}$$
$$-\sum_{lB}\frac{Z_AZ_B(R_{A\tau}-R_{l\tau}-R_{B\tau})}{|\mathbf{R}_A-\mathbf{R}_l-\mathbf{R}_B|^3}+\frac{2}{\mathcal{W}}\sum_{i\mu\alpha\beta}\int d\mathbf{k}[(D_{\mu i}^{\mathbf{k}})^*(V_{\mathbf{k}\alpha,\mathbf{k}\mu}^{\mathbf{0}A\tau})^*F'^{\mathbf{k}}_{\alpha\beta}C_{\beta i}^{\mathbf{k}}+(C_{\alpha i}^{\mathbf{k}})^*F'^{\mathbf{k}}_{\alpha\beta}V_{\mathbf{k}\beta,\mathbf{k}\mu}^{\mathbf{0}A\tau}D_{\beta i}^{\mathbf{k}}], \tag{137}$$

where E_{uc}^{HF} is the total energy per unit cell, e.g.,

$$E_{uc}^{\mathrm{HF}}=E^{\mathrm{HF}}/\mathcal{N}, \tag{138}$$

which has a finite value.

B. Hessians

The second derivative with respect to $Y_{\mathbf{k}A\tau}$ and $Y_{\mathbf{k}'A\tau}$ is given by

$$\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}=\sum_{\mathbf{k}''}\sum_{\alpha\beta}P_{\alpha\beta}^{\mathbf{k}''}[2h_{\mathbf{k}''\alpha,\mathbf{k}''\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}+2J_{\mathbf{k}''\alpha,\mathbf{k}''\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}-K_{\mathbf{k}''\alpha,\mathbf{k}''\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}]+\sum_{\mathbf{k}''}\sum_{\alpha\beta}\frac{\partial P_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}}{\partial Y_{\mathbf{k}'A'\tau'}}[2h_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}^{\mathbf{k}A\tau}$$
$$+4J_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}^{\mathbf{k}A\tau}-2K_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}^{\mathbf{k}A\tau}]-2\sum_{\mathbf{k}''}\sum_{\alpha\beta}W_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k}')\beta}S_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k}')\beta}^{\mathbf{k}'A'\tau',\mathbf{k}A\tau}$$
$$-2\sum_{\mathbf{k}''}\sum_{\alpha\beta}\frac{\partial W_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}}{\partial Y_{\mathbf{k}'A'\tau'}}S_{\mathbf{k}''\alpha,\mathbf{T}(\mathbf{k}''-\mathbf{k})\beta}^{\mathbf{k}A\tau}$$
$$+2\sum_{i\mathbf{k}''}\frac{\partial}{\partial Y_{\mathbf{k}'A'\tau'}}[\mathbf{D}^\dagger(\mathbf{V}^{-\mathbf{k}A\tau})^\dagger\mathbf{F}'\mathbf{C}+\mathbf{C}^\dagger\mathbf{F}'\mathbf{V}^{\mathbf{k}A\tau}\mathbf{D}]_{i\mathbf{k}'',i\mathbf{k}''}+\frac{\partial^2 V_{\mathrm{nuc}}}{\partial Y_{\mathbf{k}A\tau}\partial Y_{\mathbf{k}'A'\tau'}}, \tag{139}$$

where

$$P_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}(y)=\sum_I(C_{\mathbf{k}_\alpha\alpha,I}(y))^*C_{\mathbf{k}_\beta\beta,I}(y), \tag{140}$$

$$\hat{h}_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}=\frac{\partial^2}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\alpha\mathbf{k}_\alpha}|\hat{h}|\phi_{\beta\mathbf{k}_\beta}\rangle, \tag{141}$$

$$J_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}=\sum_{\gamma\theta}\sum_{\mathbf{k}}P_{\gamma\theta}^{\mathbf{k}}\frac{\partial^2}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\alpha\mathbf{k}_\alpha}\phi_{\gamma\mathbf{k}}|\phi_{\beta\mathbf{k}_\beta}\phi_{\theta\mathbf{k}}\rangle, \tag{142}$$

$$K_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}^{\mathbf{k}A\tau\mathbf{k}'A'\tau'}=\sum_{\gamma\theta}\sum_{\mathbf{k}}P_{\gamma\theta}^{\mathbf{k}}\frac{\partial^2}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}\langle\phi_{\alpha\mathbf{k}_\alpha}\phi_{\gamma\mathbf{k}}|\phi_{\theta\mathbf{k}}\phi_{\beta\mathbf{k}_\beta}\rangle, \tag{143}$$

$$W_{\mathbf{k}_\alpha\alpha,\mathbf{k}_\beta\beta}(y)=\sum_{II'}\epsilon_{II'}(y)(C_{\mathbf{k}_\alpha\alpha,I}(y))^*C_{\mathbf{k}_\beta\beta,I'}(y). \tag{144}$$

With the same procedure used in obtaining Eq. (89), we can get

$$T_l\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}=e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}_l}\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}. \tag{145}$$

Then we can conclude that

$$\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}=\delta_{-\mathbf{k}',\mathbf{k}}\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A\tau}^\dagger\partial Y_{\mathbf{k}A\tau}}. \tag{146}$$

Therefore, we only need to pay attention to the second derivatives with respect to the pairs of the symmetrized coordinates, whose reciprocal lattices have the same magnitude but different signs. From Eq. (139),

$$\frac{\partial^2 E_{uc}^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}\partial Y_{\mathbf{k}A\tau}} = \frac{1}{\mathcal{N}}\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A\tau}^{\dagger}\partial Y_{\mathbf{k}A\tau}} = \frac{1}{\mathcal{W}}\int d\mathbf{k}'\Bigg\{\sum_{\alpha\beta} P_{\alpha\beta}^{\mathbf{k}'}[2h_{\mathbf{k}'\alpha,\mathbf{k}'\beta}^{\mathbf{k}A\tau-\mathbf{k}A'\tau'} + 2J_{\mathbf{k}'\alpha,\mathbf{k}'\beta}^{\mathbf{k}A\tau-\mathbf{k}A'\tau'} - K_{\mathbf{k}'\alpha,\mathbf{k}'\beta}^{\mathbf{k}A\tau-\mathbf{k}A'\tau'}]$$

$$+\sum_{\alpha\beta}\frac{\partial P_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}}[2h_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}^{\mathbf{k}A\tau} + 4J_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}^{\mathbf{k}A\tau} - 2K_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}^{\mathbf{k}A\tau}]$$

$$-2\sum_{\alpha\beta} W_{\alpha\beta}^{\mathbf{k}'} S_{\mathbf{k}'\alpha,\mathbf{k}'\beta}^{\mathbf{k}A\tau-\mathbf{k}A'\tau'} - 2\sum_{\alpha\beta}\frac{\partial W_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}} S_{\mathbf{k}'\alpha,\mathbf{T}(\mathbf{k}'-\mathbf{k})\beta}^{\mathbf{k}A\tau}$$

$$+2\frac{\partial}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}}[\mathbf{D}^{\dagger}(\mathbf{V}^{-\mathbf{k}A\tau})^{\dagger}\mathbf{F}'\mathbf{C} + \mathbf{C}^{\dagger}\mathbf{F}'\mathbf{V}^{\mathbf{k}A\tau}\mathbf{D}]_{i\mathbf{k}',i\mathbf{k}'}\Bigg\} + \sum_{l} e^{-i\mathbf{k}\cdot\mathbf{R}_l}\frac{\partial^2}{\partial y_{0A\tau}\partial y_{lA'\tau'}}\frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_l - \mathbf{R}_B|}, \qquad (147)$$

where $Y_{\mathbf{k}A'\tau'}^{\dagger}$ is the complex conjugate of $Y_{\mathbf{k}A'\tau'}$, e.g., $Y_{-\mathbf{k}A'\tau'}$. We would like to emphasize more that there is no special difficulty for calculating second derivatives with respect to the symmetrized coordinates which break translational symmetry.

VI. APPLICATIONS OF ANALYTICAL ENERGY DERIVATIVES

A. Geometry optimization and force constants

It is well known that gradients are critical in geometry optimization and transition state searching.[32,33] The method described in the previous sections provides an efficient and accurate way to obtain them and then can greatly enhance the capability of *ab initio* methods to handle extended systems.

Since the HF method or other methods such as DFT can only deal with periodic systems when the number of the nuclei is infinite, there is no way to obtain the force constants for the movements concerning an individual nucleus and the interatomic force constants, which are required in the prediction of dynamical properties of solids and critical in understanding reaction mechanisms of biopolymers. The analytical procedure described in the previous sections provides a way to calculate the whole spectrum of the force constants with respect to the symmetrized coordinates. With them, we can, indeed, calculate the force constants for the movements concerning an individual nucleus and interatomic force constants.

Let us consider the interatomic force constants for nucleus A in the lth unit cell and nucleus A' in the l'th unit cell. From Eqs. (86) and (88), we obtain

$$F_{l'A'\tau',lA\tau} = \frac{\partial^2 E^{\mathrm{HF}}}{\partial y_{l'A'\tau'}\partial y_{lA\tau}}$$

$$= \frac{1}{\mathcal{N}^2}\sum_{\mathbf{k}'} e^{-\mathbf{k}'\cdot\mathbf{R}_{l'}}\sum_{\mathbf{k}} e^{-\mathbf{k}\cdot\mathbf{R}_l}\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}$$

$$= \frac{1}{\mathcal{N}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_{l'}-\mathbf{R}_l)}\frac{\partial^2 E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}\partial Y_{\mathbf{k}A\tau}}$$

$$= \frac{1}{\mathcal{W}}\int \frac{\partial^2 E_{uc}^{\mathrm{HF}}}{\partial Y_{\mathbf{k}A'\tau'}^{\dagger}\partial Y_{\mathbf{k}A\tau}} e^{i\mathbf{k}\cdot(\mathbf{R}_{l'}-\mathbf{R}_l)} d\mathbf{k}. \qquad (148)$$

By letting $l = l'$ and $A = A'$, we can get force constants for each individual nucleus.

B. Phonon disperson curves

From the force constants with respect to symmetrized coordinates, we can calculate the phonon dispersion curves, which offer substantial information in determining the heat, optical, and mechanic properties of extended systems such as heat capacity, heat expansion, infrared and Raman spectroscopy, nonlinear optical properties, and even high temperature superconductivity.

From Eqs. (86) and (88), we can see that the transformation from Cartesian coordinates, $\{y_{lA\tau}\}$, to symmetrized coordinates is not unitary. In fact, the space is scaled by a factor of $1/\mathcal{N}$. This means the velocities of an object and force constants in the two spaces are different, scaled by some factors. To get correct kinetic and potential energies, we need to introduce the normalized symmetrized coordinates by

$$\overline{Y}_{\mathbf{k}A\tau} = \sqrt{\mathcal{N}} Y_{\mathbf{k}A\tau} = \frac{1}{\sqrt{\mathcal{N}}}\sum_{l} e^{-i\mathbf{k}\cdot\mathbf{R}_l} y_{lA\tau}. \qquad (149)$$

$y_{lA\tau}$ can then be expressed as

$$y_{lA\tau} = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_l} Y_{\mathbf{k}A\tau} = \frac{1}{\sqrt{\mathcal{N}}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_l}\overline{Y}_{\mathbf{k}A\tau}. \qquad (150)$$

It is easy to check that the transformations between the two sets of coordinates are unitary.

Using Eqs. (149) and (150), the kinetic energy of an extended system with periodicity at a stable structure can be expressed as

$$T=\frac{1}{2}\sum_{lA\tau}\dot{y}_{lA\tau}M_A\dot{y}_{lA\omega}$$
$$=\frac{1}{2}\sum_{lA\tau}\sum_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_l}\dot{Y}^{\dagger}_{\mathbf{k}'A\tau}M_A\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{R}_l}\dot{Y}_{\mathbf{k}A\tau}$$
$$=\frac{\mathcal{N}}{2}\sum_{A\tau}\sum_{\mathbf{k}}\dot{Y}^{\dagger}_{\mathbf{k}A\tau}M_A\dot{Y}_{\mathbf{k}A\tau}$$
$$=\frac{1}{2}\sum_{A\tau}\sum_{\mathbf{k}}\dot{\bar{Y}}^{\dagger}_{\mathbf{k}A\tau}M_A\dot{\bar{Y}}_{\mathbf{k}A\tau}, \tag{151}$$

where the dots above the coordinates means the derivatives with respect to time. Around the stable structure, the potential energy which is correct to second-order of the displacements is given by

$$V=\frac{1}{2}\sum_{l'A'\tau'}\sum_{lA\tau}y_{l'A'\tau'}\frac{\partial^2E^{\mathrm{HF}}}{\partial y_{l'A'\tau'}\partial y_{lA\tau}}y_{lA\tau}$$
$$=\frac{1}{2\mathcal{N}^2}\sum_{l'A'\tau'}\sum_{lA\tau}\sum_{\mathbf{k}'\mathbf{k}}y_{l'A'\tau'}e^{-i(\mathbf{k}'\cdot\mathbf{R}_l'-\mathbf{k}\cdot\mathbf{R}_l)}$$
$$\times\frac{\partial^2E^{\mathrm{HF}}}{\partial Y_{\mathbf{k}'A'\tau'}\partial Y_{\mathbf{k}A\tau}}y_{lA\tau}$$
$$=\frac{1}{2}\sum_{A'\tau'}\sum_{A\tau}\sum_{\mathbf{k}}Y^{\dagger}_{\mathbf{k}A'\tau'}\frac{\partial^2E^{\mathrm{HF}}}{\partial Y^{\dagger}_{\mathbf{k}A'\tau'}\partial Y_{\mathbf{k}A\tau}}Y_{\mathbf{k}A\tau}$$
$$=\frac{1}{2}\sum_{A'\tau'}\sum_{A\tau}\sum_{\mathbf{k}}\bar{Y}^{\dagger}_{\mathbf{k}A'\tau'}\frac{\partial^2E^{\mathrm{HF}}_{uc}}{\partial Y^{\dagger}_{\mathbf{k}A\tau}\partial Y_{\mathbf{k}A\tau}}\bar{Y}_{\mathbf{k}A\tau}, \tag{152}$$

where Eqs. (149) and (150) have been used. Then the vibrational frequencies $\omega(\mathbf{k})$ or the phonon dispersions are determined by

$$\mathrm{Det.}|\{M_{A'}^{-1/2}\mathbf{F}(\mathbf{k})_{A'\tau',A\tau}M_A^{-1/2}\}-\omega(\mathbf{k})^2\mathbf{I}|=0, \tag{153}$$

where

$$\{\mathbf{F}_X(\mathbf{k})\}_{A'\tau',A\tau}=\frac{\partial^2E^{\mathrm{HF}}}{\partial\bar{Y}^{\dagger}_{\mathbf{k}A'\tau'}\partial\bar{Y}_{\mathbf{k}A\tau}}=\frac{\partial^2E^{\mathrm{HF}}_{uc}}{\partial Y^{\dagger}_{\mathbf{k}A'\tau'}\partial Y_{\mathbf{k}A\tau}}. \tag{154}$$

Since second derivatives with respect to any symmetrized coordinate and its conjugate can be easily evaluated, the method developed above has the capability to determine the phonon dispersion curves in the whole Brillouin zone. Furthermore, the computational cost for calculating the phonon spectrum with a reciprocal lattice $\mathbf{k}\neq 0$ is the same as that needed for $\mathbf{k}=0$ where the translational symmetry is preserved.

When $\mathbf{k}=0$, the force constant matrix is

$$\{\mathbf{F}_X(\mathbf{0})\}_{A'\tau',A\tau}=\frac{\partial^2E^{\mathrm{HF}}_{uc}}{\partial y_{A'\tau'}\partial y_{A\tau}}, \tag{155}$$

which can be calculated by finite differences of energies at the points around the stable geometry. We recently have calculated the vibrational frequencies of polymethineimine for $\mathbf{k}=0$ with numerical Hessians using second-order many-body perturbation theory.[27]

VII. CONCLUSIONS

We have given a systematic study and developed an effective procedure for analytical evaluation of energy derivatives in extended systems. The procedure not only greatly improves the performance of the calculations of the derivatives compared to the finite difference method, but it also enables us to calculate energy derivatives with respect to any displacement, including those which break the translational symmetry.

By using semisymmetric orbitals and the procedure recently developed by us,[17] we can eliminate the linear dependence among basis functions, which is an unavoidable problem in the analytical evaluation of energy derivatives for extended systems, and get a set of independent, semiorthogonal basis functions, their derivatives, and the derivatives of their overlap matrix.

By introducing symmetrized coordinates for nuclei, the derivatives of the overlap, the Fock, and the coefficient matrices become blocked. Then the derivatives of the independent orbitals and their overlap matrix can be easily calculated since the infinite summations are eliminated. With the symmetrized coordinates, the CPHF equations only couple those which preserve quasimomentum. The equations can be easily solved and require no extra effort for the displacements which break the translational symmetry.

The explicit expressions for analytical gradients and Hessians of the HF energy have been derived for extended systems. It is shown that the gradient has nonzero components only along the displacements, which keeps the translational symmetry. With symmetrized coordinates, the Hessian becomes block diagonal.

With second derivatives of the electronic energy with respect to symmetrized coordinates, one can calculate force constants for individual nuclei, interatomic force constants, and phonon dispersion curves in the whole Brillouin zone. The computational cost to calculate the phonon spectrum with $\mathbf{k}\neq 0$ in the Brillouin zone is the same as that needed for the spectrum at $\mathbf{k}=0$.

The method developed in this paper can also be applied to DFT and there is no special difficulty to get the expressions for derivatives of correlated energies.

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