Real-space density functional perturbation theory for phonons

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We present a real-space formulation and implementation of density functional perturbation theory for the calculation of phonons. Specifically, employing a local form for the electrostatics, we derive expressions for the dynamical matrix and associated Sternheimer equation at any arbitrary phonon wavevector in the framework of real-space Kohn-Sham density functional theory. In particular, the formulation is applicable to insulating as well as metallic systems of any dimensionality, for both orthogonal and non-orthogonal cells, in the context of local exchange-correlation functionals and the Kleinman-Bylander representation for nonlocal pseudopotentials. We also develop an implementation of the proposed formulation within the real-space high-order finite-difference method. Through representative examples, we verify the accuracy of the developed formulation and implementation, showing excellent agreement with established plane-wave results.

I. INTRODUCTION

Kohn-Sham density functional theory (DFT) [1, 2] has firmly established itself as one of the cornerstones of materials and chemical sciences research, providing a framework for understanding and predicting materials properties from the first principles of quantum mechanics, without any empirical or ad hoc parameters, all at an affordable computational cost. The widespread use of DFT can be attributed to its generality, simplicity, and high accuracy to cost ratio relative to other such ab initio methods. Though less computationally demanding than wavefunction-based alternatives, the efficient solution of the Kohn-Sham problem remains a challenging task, scaling cubically with system size, and with a large prefactor. One situation where this bottleneck can manifest itself is the study of the system’s response to perturbations — many physical properties can be so computed — where the translational symmetry/periodicity of the system can be broken, limiting the use of the standard Kohn-Sham DFT formalism developed for crystals.

Density functional perturbation theory (DFPT) [3–6] is an elegant and efficient ab initio approach for determining the response of materials systems to perturbations in the context of electronic structure calculations, typically within the Kohn-Sham formalism, thus circumventing the need for large supercells and/or a series of ground state calculations involving the unperturbed and perturbed systems. The perturbations that have been formulated in the framework of DFPT thus far include atomic vibrations [4, 5], strain [7, 8], strain gradient [9, 10], electric field [11, 12], and magnetic field [13, 14]; which have found a number of applications including structural stability [15, 16], elastic moduli [17, 18], flexoelectric coefficients [19, 20], Raman spectra [21, 22], electro-optic coupling [23, 24], ferroelectric and ferroelastic transitions [25, 26], transport properties such as temperature-dependent phonon-limited electrical and thermal conductivity [27], and thermodynamic properties such as specific heat [28, 29] and thermal expansion [30, 31].

Phonons describe the vibrational/dynamic behavior of the crystal within the adiabatic harmonic approximation [3]. Mathematically, they represent the response of the system to atomic vibrations, which can be described by the standard eigenproblem associated with the dynamical matrix, i.e., Hessian/second derivative of the energy with respect to atomic positions, with the matrix entries appropriately scaled by the atomic masses. In particular, the eigenvalues and eigenvectors of the dynamical matrix represent the phonon frequencies and modes, respectively. Phonons play a significant role in determining a number of the aforementioned properties/behavior that cannot be described by static models, including structural instability, thermal conductivity, heat capacity, coefficients of thermal expansion, and superconductivity [3]. This motivates the development of formulations and implementations that can calculate the phonon spectra for materials systems from first principles, which is the focus of this work.

The calculation of phonons in the context of DFT has its origins in Ref. [32], where a dielectric approach for the calculation of the Born-von Karman force constants was proposed. However, this approach is limited to local perturbations and requires the inversion of the large matrices. Thereafter, the frozen-phonon method was introduced [33], wherein elements of the dynamical matrix are computed using numerical approximations to the derivatives, i.e., energy/force differences between perturbed and equilibrium atomic configurations. However, this method is particularly expensive, requiring large supercells to capture low frequency vibrations. As an alternative to these static methods, the vibrational properties can be also be extracted from molecular dynamics simulations [34], wherein time averages over the atomic trajectories can be used to compute the phonon spectra. However, such an approach is even more expensive, requiring large numbers of time steps, and also requiring large supercells to capture low frequency vibrations. This has motivated the development of perturbative approaches [4, 6, 35] — represent some of the first few instances of DFPT — wherein the phonon wavevector-characterized atomic perturbations enables the calculation of the dynamical matrix at arbitrary wavevectors on the unit cell/fundamental domain. However, even with these significant advances, phonon calculations are extremely expensive, scaling quartically with system size (assuming
sufficiently fast decay in the dynamical matrix), and with a very large prefactor.

The current formulations and implementations of DFPT for phonons are restricted to the planewave method [4, 36–45], which is among the most widely used techniques for the solution of the Kohn-Sham problem [43–50]. However, the Fourier basis is global, which limits scalability on parallel machines; and it is also periodic, whereby lower dimensional systems such as surfaces and nanowires require the introduction of artificial periodicity, which can necessitate the use of large vacuum regions. The limitations of the planewave method have motivated the development of a number of alternative techniques using systematically improvable, localized representations [51–71], among which real-space finite-difference methods [72, 73] are likely the most mature and widely used. In particular, real-space methods can efficiently leverage large-scale parallel computational resources [56, 67, 74–76], resulting in substantially reduced solution times for the electronic ground state compared to established planewave codes [68, 76]; and can naturally accommodate periodic as well as Dirichlet boundary conditions, and combinations thereof, enabling the efficient and accurate treatment of semi-infinite and bulk systems alike. However, in spite of significant advances, a real-space formulation of DFPT for phonons, which can naturally handle systems of any dimensionality, and has the potential to enable significantly faster and larger simulations, has not been developed heretofore.

In this work, as the first step towards real-space DFPT for a variety of perturbations, we present a real-space formulation and implementation for the calculation of phonons. Specifically, employing a local form for the electrostatics [77–79], local exchange-correlation functional [2], and Kleinman-Bylander [80] representation for the nonlocal pseudopotential, we derive expressions for the dynamical matrix and associated Sternheimer equation at any arbitrary positions of the nuclei. In the frozen-core pseudopotential approximation [81], the finite-temperature Kohn-Sham free energy [2, 82] at the electronic ground state can be decomposed as:

\[
E_{KS}(\mathbf{R}) = T_s(\mathbf{R}) + E_{xc}(\mathbf{R}) + E_{el}(\mathbf{R}) + E_{nl}(\mathbf{R}) + E_{ent}(\mathbf{R}),
\]

where \(T_s\), \(E_{xc}\), \(E_{el}\), \(E_{nl}\), and \(E_{ent}\) are the electronic kinetic energy, exchange-correlation energy, electrostatic energy, nonlocal pseudopotential energy, and electronic entropic energy, respectively. Neglecting spin and adopting a local real-space formulation for the electrostatics [77–79], local density approximation (LDA) [2] for the exchange-correlation energy, and Kleinman-Bylander [80] form for the nonlocal pseudopotentials, the energy components in Eq. 1 can be expanded as:

\[
T_s(\mathbf{R}) = -\sum_{n=1}^{N} g_n(\mathbf{R}) \int_{\Omega} \psi_n^*(x, \mathbf{R}) \nabla^2 \psi_n(x, \mathbf{R}) \, dx,
\]

\[
E_{xc}(\mathbf{R}) = \int_{\Omega} \varepsilon_{xc}(\rho(x, \mathbf{R})) \rho(x, \mathbf{R}) \, dx,
\]

\[
E_{el}(\mathbf{R}) = \frac{1}{2} \int_{\Omega} (\rho(x, \mathbf{R}) + b(x, \mathbf{R})) \phi(x, \mathbf{R}) \, dx
\]

\[
+ \frac{1}{2} \int_{\Omega} \left( b(x, \mathbf{R}) + \tilde{b}(x, \mathbf{R}) \right) V_{el}(x, \mathbf{R}) \, dx - \frac{1}{2} \sum_{j=1}^{N} \int_{\Omega} \tilde{b}_j(x, \mathbf{R}_j) \tilde{V}_j(x, \mathbf{R}_j) \, dx,
\]

\[
E_{nl}(\mathbf{R}) = 2 \sum_{n=1}^{N} g_n(\mathbf{R}) \sum_{j=1}^{N} \sum_{p=1}^{P_j} \gamma_{j,p} \int_{\Omega} \left| \psi_n^*(x, \mathbf{R}) \chi_{j,p}(x, \mathbf{R}_j) \right|^2 \, dx,
\]

\[
E_{ent}(\mathbf{R}) = 2k_B T \sum_{n=1}^{N} \left( g_n(\mathbf{R}) \log g_n(\mathbf{R}) + (1 - g_n(\mathbf{R})) \log(1 - g_n(\mathbf{R})) \right),
\]

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Finally, we provide concluding remarks in Section V.
where \( \rho \) is the electron density:

\[
\rho(x, R) = 2 \sum_{n=1}^{N_e} g_n(R) |\psi_n(x, R)|^2 ;
\]

\( \{\psi_n\}_{n=1}^{N_e} \) are the Kohn-Sham orbitals with occupations \( \{g_n\}_{n=1}^{N_e} \); \( \varepsilon_{xc} \) is the exchange-correlation energy per particle; \( b = \sum_{j=1}^{N} b_j \) is the total ionic pseudocharge density, with \( \{b_j = -\frac{1}{4\pi} \nabla^2 V_j\}_{j=1}^{N} \) being the individual spherically-symmetric pseudocharge densities corresponding to the local part of the pseudopotentials \( \{V_j\}_{j=1}^{N} \); \( \tilde{b} = \sum_{j=1}^{N} \tilde{b}_j \) is the total reference pseudocharge density, with \( \{\tilde{b}_j = -\frac{1}{4\pi} \nabla^2 \tilde{V}_j\}_{j=1}^{N} \) being the individual spherically-symmetric reference pseudocharge densities corresponding to the reference potentials \( \{\tilde{V}_j\}_{j=1}^{N} \); \( \phi \) is the electrostatic potential; \( E_{xc} \) is the self-interaction and overlap correction energy; \( \{\{\chi_{J,p}\}_{p=1}^{P_J}\}_{J=1}^{N} \) are the nonlocal pseudopotential projectors with normalization constants \( \{\{\gamma_{J,p}\}_{p=1}^{P_J}\}_{J=1}^{N} \); \( k_B \) is the Boltzmann constant, and \( T \) is the electronic temperature.

The ground state orbitals \( \{\psi_n\}_{n=1}^{N_e} \), occupations \( \{g_n\}_{n=1}^{N_e} \), and electrostatic potential \( \phi \) are solutions to the following equations [68]:

\[
\begin{align*}
\left( \mathcal{H}(R) = -\frac{1}{2} \nabla^2 + V_{xc}(\rho(R)) + \phi(R) + V_{nl}(R) \right) \psi_n(x, R) &= \lambda_n(R) \psi_n(x, R) \quad (8) \\
g_n(R) &= \left( 1 + \exp \left( \frac{\lambda_n(R) - \lambda_F(R)}{k_B T} \right) \right)^{-1}, \quad \lambda_F(R) \text{ is s.t. } 2 \sum_{n=1}^{N_e} g_n(R) = N_e, \quad (9) \\
-\frac{1}{4\pi} \nabla^2 \phi(x, R) &= \rho(x, R) + b(x, R), \quad (10)
\end{align*}
\]

where \( \mathcal{H} \) denotes the Hamiltonian, \( \lambda_n \) are the Kohn-Sham eigenvalues, \( \lambda_F \) is the Fermi level, \( N_e \) is the total number of electrons, \( V_{xc} \) is the exchange-correlation potential:

\[
V_{xc}(\rho(R)) = \frac{\delta E_{xc}(\rho(R))}{\delta \rho(R)} = \varepsilon_{xc}(\rho(R)) + \rho(R) \frac{\partial \varepsilon_{xc}(\rho(R))}{\partial \rho(R)}, \quad (11)
\]

and \( V_{nl} \) is the nonlocal pseudopotential operator:

\[
V_{nl}(R) = \sum_{J=1}^{N} \sum_{p=1}^{P_J} \gamma_{J,p} |\chi_{J,p}(R)|^2 \langle \chi_{J,p}(R) | \chi_{J,p}(R) \rangle. \quad (12)
\]

At this electronic ground state, for an equilibrium atomic configuration, the phonon spectrum corresponding to vibrations of the system can be calculated, as described in the next section.

### III. REAL-SPACE DFPT: PHONONS

We now present a real-space formulation of DFPT for the calculation of phonons within the framework outlined in the previous section. In particular, we summarize the formulation here, the details of which along with the derivation for all the expressions can be found in Appendix A. We start by introducing the dynamical matrix \( D \), which can be defined within the adiabatic harmonic approximation [83] as:

\[
D_{I\alpha,J\beta}(R) = \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E_{KS}(R)}{\partial R_{I\alpha} \partial R_{J\beta}}, \quad I, J = 1, 2, \ldots N, \quad \alpha, \beta = 1, 2, 3, \quad (13)
\]

where \( E_{KS} \) is the ground state Kohn-Sham energy presented in Eq. 1, and \( \{M_I\}_{I=1}^{N} \) are the masses of the atoms located at \( \{R_I = (R_{I1}, R_{I2}, R_{I3})\}_{I=1}^{N} \). Though the focus below is on phonons, the formulation is equally applicable to the calculation of vibrational spectra for isolated systems/molecules, as demonstrated in Appendix B.

Let \( \Omega \) have additional translational symmetry within it, i.e., there exists a unit cell/fundamental domain \( \Omega \) with lattice vectors \( \mathbf{L}_1, \mathbf{L}_2, \) and \( \mathbf{L}_3 \), such that the number of unit cells within \( \Omega \) is \( N_e \), each with \( \bar{N} \) atoms. Exploiting
this symmetry, the dynamical matrix can be block diagonalized to arrive at the matrix $\tilde{D}$, also referred here to as the dynamical matrix, to be consistent with the terminology adopted in literature [3]:

$$
\tilde{D}_{\alpha J}(q, R) = \frac{1}{\sqrt{M_I M_J}} \left[ \frac{1}{\hbar^2} \sum_{n=1}^{N(a)} \sum_{\alpha \beta} e^{i q_n (L_{\alpha b} - L_{\beta b})} \left( \frac{\partial^2 E_{KS}(R)}{\partial R^a_\alpha \partial R^b_\beta} \right) \right], \quad I, J = 1, 2, \ldots N, \quad \alpha, \beta = 1, 2, 3,
$$

where $q = (q_1, q_2, q_3)$ is the phonon wavevector, i.e., the indexing used to label the block diagonalized dynamical matrix, $L_a = a_1 L_1 + a_2 L_2 + a_3 L_3$ is used to denote the translation vector from $\Omega$ to any equivalent unit cell within $\Omega$ that is indexed by the set of integers $\{a_1, a_2, a_3\}$, $\sum_n$ is sum over all such translation vectors, and $R^a_\alpha$ is the $\alpha$th coordinate of the $I$th atom in the $\alpha$th unit cell. In the framework of the real-space Kohn-Sham DFT formalism outlined in Section II and its translational symmetry-adapted version on $\Omega$ [68] — orbitals and related quantities are restricted to the unit cell $\Omega$ through the introduction of the $k$ wavevector — the dynamical matrix is derived to be:

$$
\tilde{D}_{\alpha J}(q, R) = \frac{1}{\sqrt{M_I M_J}} \left[ -2 \int_{\Omega} N_{\alpha}^{(k)}(R, k) \left\{ \int_{\Omega} \psi^{(1)*}_n(x, R, k) \hat{H}_{\alpha J}(R, k, q) \psi_n(x, R, k) \, dx \right\} 
+ \int_{\Omega} \psi^{(1)*}_n(x, R, -k, q) \hat{H}_{\alpha J}(R, -k, q) \psi_n(x, R, k) \, dx \right] 
+ \int_{\Omega} \rho^{(1)*}_n(x, R, q) \left( \frac{1}{2} \int_{\Omega} (\rho^{(1)*}_n(x, R, q) + \rho^{(1)*}_n(x, -R, q)) \, dx \right) 
- \delta_{IJ} \int_{\Omega} \sum_a e^{-i q \cdot L_a} \left( \nabla_{\alpha} b_j(x, R^\alpha) - \nabla_{\beta} b_j(x, R^\beta) \right) \sum_b e^{i q \cdot L_b} \left( \nabla_{\beta} \tilde{V}_j(x, R^\beta) - \nabla_{\alpha} \tilde{V}_j(x, R^\alpha) \right) \, dx
+ \frac{1}{2} \int_{\Omega} \sum_{\alpha} e^{-i q \cdot L_a} \left( \nabla_{\alpha} b_j(x, R^\alpha) + \nabla_{\beta} b_j(x, R^\beta) \right) \sum_{\beta} e^{-i q \cdot L_b} \left( \nabla_{\alpha} \tilde{V}_j(x, R^\alpha) - \nabla_{\beta} \tilde{V}_j(x, R^\beta) \right) \, dx
- \frac{1}{2} \int_{\Omega} \nabla_{\alpha} \left( b(x, R) + \tilde{b}(x, R) \right) \left( \nabla_{\beta} \tilde{V}_j(x, R^\beta) - \nabla_{\beta} \tilde{V}_j(x, R^\beta) \right) \, dx
- \frac{2}{\Omega} \int_{\Omega} N_{\alpha}^{(k)}(R, k) \sum_{p,j} \gamma_{n,p} \left( \sum_{\alpha} \left( \int_{\Omega} \psi^{(1)*}_n(x, R, k) \psi_n(x, R, k) \, dx \right) \right) 
\times \sum_{\alpha} \left( \sum_{\alpha} \left( \int_{\Omega} \chi^{(1)*}_{\alpha p}(x, R^\alpha) \psi_n(x, R, k) e^{-i k \cdot L_{\alpha d}} \, dx \right) \right) + 2g_{n J}(R, k, q) \sum_{p,j} \gamma_{n,p} \left( \sum_{\alpha} \left( \int_{\Omega} \psi^{(1)*}_n(x, R, k) \psi_n(x, R, k) \, dx \right) \right) 
\times e^{i k \cdot L_{\alpha d}} \nabla_{\alpha} \chi_{n,p}(x, R^\alpha) \, dx \right) \sum_{\alpha} \left( \sum_{\alpha} \left( \int_{\Omega} \chi^{(1)*}_{\alpha p}(x, R^\alpha) \psi_n(x, R, k) e^{-i k \cdot L_{\alpha d}} \, dx \right) \right) - 2g_{n J}(R, k, q) \delta_{IJ} \sum_{\alpha} \left( \int_{\Omega} \psi^{(1)*}_n(x, R, k) \psi_n(x, R, k) e^{-i k \cdot L_{\alpha d}} \, dx \right)
$$
\begin{align}
&\times \chi_{I:p}(x, R^c_k) \sum_d \left( \int_{\Omega} \nabla_{\alpha I:p}(x, R^d_k) \psi_n(x, R, k) e^{-i k L_d} \, dx \right) + g_n(R, k) \sum_{p=1}^{P_I} \gamma_{I:p} \\
&\times \left( \sum_c \left( \int_{\Omega} \psi_n^{(1) *} (x, R, k, q) e^{i (k+q) L_e} \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \nabla_\beta \chi_{I:p}(x, R^d_{I}) \psi_n(x, R, k) e^{-i k L_d} \, dx \right) \\
&+ \sum_c \left( \int_{\Omega} \psi_n^{(1) *} (x, R, k, q) e^{i k L_e} \nabla_\beta \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \nabla_\alpha \chi_{I:p}(x, R^d_{I}) \psi_n^{(1) *} (x, R, k, q) e^{-i (k+q) L_d} \, dx \right) \\
&+ g_n(R, k) \sum_{p=1}^{P_I} \gamma_{I:p} \left( \sum_c \left( \int_{\Omega} \psi_n^{(1) *} (x, R, -k, q) e^{-i (k+q) L_e} \nabla_\beta \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \nabla_\alpha \chi_{I:p}(x, R^d_{I}) \psi_n^{(1) *}(x, R, k, q) \, dx \right) \\
&\times \psi_n(x, R, k) e^{-i k L_d} \, dx \right) \\
&+ g_n(R, k) \sum_{p=1}^{P_I} \gamma_{I:p} \left( \sum_c \left( \int_{\Omega} \psi_n^{(1) *} (x, R, q) e^{i (k+q) L_e} \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \nabla_\alpha \chi_{I:p}(x, R^d_{I}) \psi_n^{(1) *}(x, R, k, q) \, dx \right) \\
&\times \psi_n(x, R, k, q) e^{-i k L_d} \, dx \right) \\
&+ \sum_d \left( \int_{\Omega} \chi_{I:p}(x, R^d_{I}) \psi_n(x, R, k, q) e^{-i k L_d} \, dx \right) + \sum_c \left( \int_{\Omega} \chi_{I:p}^{(1) *}(x, R, q) e^{i (k+q) L_e} \nabla_\beta \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \chi_{I:p}(x, R^d_{I}) \psi_n^{(1) *}(x, R, -k, q) \, dx \right) \\
&\times \psi_n(x, R, k) e^{-i k L_d} \, dx \right) \\
&+ \sum_d \left( \int_{\Omega} \nabla_\beta \chi_{I:p}^{(1) *}(x, R^d_{I}) \psi_n(x, R, k) e^{-i k L_d} \, dx \right) + \sum_c \left( \int_{\Omega} \nabla_\alpha \chi_{I:p}^{(1) *}(x, R, q) e^{i (k+q) L_e} \chi_{I:p}(x, R^e_{I}) \, dx \right) \sum_d \left( \int_{\Omega} \nabla_\beta \chi_{I:p}(x, R^d_{I}) \psi_n^{(1) *}(x, R, -k, q) \, dx \right) \\
&\times \psi_n(x, R, k) e^{-i k L_d} \, dx \right) \\
&\times \psi_n(x, R, k, q) e^{-i k L_d} \, dx \right) \\
&+ 2kBT \int_k \sum_{n=1}^{N_{v,k}} \left\{ g_n^{(1)}(R, k, q) g_n^{(1)}(R, k, q) \left( \frac{1}{g_n(R, k)} (1 - g_n(R, k)) \right) \right\} \, dk ,
\end{align}

where $\Re$ denotes the real-part of the expression, $\delta$ is the Kronecker delta, $f_k$ represents the volume average over the Brillouin zone, $N_v(k)$ is the number of states associated with the wavevector $k$, and

$$
\mathcal{H}^{(1)}_{I:a}(R, k, q) = \left( 2 \frac{\partial \varepsilon_{xc}(R)}{\partial \rho(R)} + \rho(R) \frac{\partial^2 \varepsilon_{xc}(R)}{\partial (\rho(R))^2} \right) \rho^{(1)}_{I:a}(R, q) + \phi^{(1)}_{I:a}(R, q)
\end{align}

- \sum_{p=1}^{P_I} \gamma_{I:p} \sum_a e^{i(k+q) L_a} |\nabla_\alpha \chi_{I:p}(R^e_a)| \sum_b \langle \chi_{I:p}(R^b) \rangle |e^{-i k L_b} |
\end{align}

$$
\rho^{(1)}_{I:a}(x, R, k, q) = 2 \int_k \sum_{n=1}^{N_{v,k}} \left( g_n^{(1)}(R, k, q) \right) |\psi_n(x, R, k)|^2 + g_n(R, k) \psi_n^{*}(x, R, k) \psi_n^{(1)}_{I:a}(x, R, k, q)
\end{align}

$$
\psi_n^{(1)}(x, R, k) = - \frac{g_n(R, k) (1 - g_n(R, k))}{k_B T} \delta_{q0} \int_{\Omega} \psi_n^{*}(x, R, k) \mathcal{H}^{(1)}_{I:a}(R, k, q) \psi_n(x, R, k) \, dx.
\end{align}
In addition, $\phi^{(1)}_{I_\alpha}$ is the solution of the Poisson problem:

$$-rac{1}{4\pi} \nabla^2 \phi^{(1)}_{I_\alpha}(x, R, q) = \rho^{(1)}_{I_\alpha}(x, R, q) + b^{(1)}_{I_\alpha}(x, R, q) , \quad (22)$$

$$\phi^{(1)}_{I_\alpha}(x + L_j, R, q) = e^{i q \cdot L_j} \phi^{(1)}_{I_\alpha}(x, R, q) , \quad j = 1, 2, 3 , \quad (23)$$

and $\psi^{(1)}_{n_{I_\alpha}}$ is the solution of the Sternheimer equation [3, 84]:

$$\left( H(R, k + q) + Q(R, k + q) - \lambda_n(R, k) I \right) \psi^{(1)}_{n_{I_\alpha}}(x, R, q) = \left( P_n(R, k + q) - I \right) H^{(1)}_{I_\alpha}(R, k, q) \psi^{(1)}_{n_{I_\alpha}}(x, R, k) , \quad (24)$$

$$\psi^{(1)}_{n_{I_\alpha}}(x + L_j, R, k, q) = e^{i(q + k) \cdot L_j} \psi^{(1)}_{n_{I_\alpha}}(x, R, k, q), \quad j = 1, 2, 3 , \quad (25)$$

where the operators

$$Q = \sum_{m=1}^{N_s} \gamma_m |\psi_m|^2 |\psi_m| , \quad P_n = \sum_{m=1}^{N_s} \zeta_{n,m} |\psi_m|^2 |\psi_m| , \quad (26)$$

have been introduced to remove the singularity inherent to the Sternheimer equation [3], with the coefficients $\{\gamma_m\}_{m=1}^{N_s}$ taking arbitrary values, and

$$\zeta_{n,m} = \begin{cases} 
\frac{\delta_{q0} + (1 - \delta_{q0}) \left( 1 - \gamma_m \left[ 1 - \frac{1 - \delta_{q0} \lambda_n(R, k)}{2 \delta_{q0}} \right] \right)}{\lambda_n(R, k) \gamma_m - \lambda_m(R, k + q)}, & \text{if } m = n \& \lambda_n(R, k) = \lambda_m(R, k + q), \\
1 - \gamma_m \left[ 1 - \frac{1 - \delta_{q0} \lambda_n(R, k)}{2 \delta_{q0}} \right], & \text{if } m \neq n \& \lambda_n(R, k) = \lambda_m(R, k + q), \\
\frac{\gamma_m}{\lambda_n(R, k) - \lambda_m(R, k + q)}, & \text{otherwise}. \end{cases} \quad (27)$$

Similar to the Kohn-Sham eigenproblem (Eq. 8), the Sternheimer equation (Eq. 24) is nonlinear and needs to be solved self-consistently. This is typically done using a fixed-point iteration with respect to $\rho^{(1)}_{I_\alpha}$, i.e., for a given $\rho^{(1)}_{I_\alpha}$, $\phi^{(1)}_{I_\alpha}$ is calculated by solving the Poisson problem in Eq. 22, $H^{(1)}_{I_\alpha}$ is then calculated using Eq. 16, $\psi^{(1)}_{n_{I_\alpha}}$ is then calculated by solving the Sternheimer equation in Eq. 24, $\rho^{(1)}_{I_\alpha}$ is then calculated using Eq. 20 with input from Eqs. 20 and 21, after which the above process is repeated, until a self-consistent solution is obtained. Note that in the current formulation for the Sternheimer equation, as in previous such formulations [3, 85], it is assumed that $k + q$ and $-k + q$ lie in the wavevector space spanned by $k$. Though this is always true in the continuous setting, in practical implementations/calculations it needs to be ensured that sampled wavevectors $k$ and $q$ are such that $k + q$ and $-k + q$ are a part of the chosen $k$ wavevectors. Indeed, this restriction is only for the calculation of the dynamical matrix and not for the electronic/structural ground state.

The formulation presented above is applicable to nonorthogonal unit cells, provided all the gradients appearing in the expressions are interpreted as derivatives along the orthogonal Cartesian directions. Alternatively, the gradients can be evaluated with respect to the lattice vector directions, as typically done for convenience within implementations, and the resultant dynamical matrix can be transformed as follows:

$$\tilde{D}_{I,J}(q, R) := W^T \tilde{D}_{I,J}(q, R_l) W , \quad W = \begin{bmatrix}
\tilde{L}_{11} & \tilde{L}_{12} & \tilde{L}_{13} \\
\tilde{L}_{21} & \tilde{L}_{22} & \tilde{L}_{23} \\
\tilde{L}_{31} & \tilde{L}_{32} & \tilde{L}_{33}
\end{bmatrix}^{-1} , \quad (28)$$

where $\tilde{D}_{I,J}$ is a $3 \times 3$ sub-matrix of $\tilde{D}$ with components $\tilde{D}_{I,J,\alpha,\beta}$, $\alpha, \beta = 1, 2, 3$. In addition, $\tilde{L}_j = L_j / |L_j|$, $j = 1, 2, 3$, and $R_l$ are the atom coordinates with respect to these unit vectors.

The above formulation is also applicable to systems of any dimensionality, i.e., crystals, surfaces, and wires, since being in real-space, it allows for periodic, Bloch-periodic, and Dirichlet boundary conditions, and combinations thereof, to be specified. Indeed, for quasi 2D and 1D systems, the vectors $k$, $q$, and $L_l$ need to be suitably redefined with two and one components, respectively. Also, the boundary conditions on $\phi^{(1)}_{I_\alpha}$ presented in Eq. 22 are for the direction(s) along which the system is extended. For the direction(s) along which the system is finite, the appropriate Dirichlet boundary conditions need to be prescribed, as done in Kohn-Sham DFT for the electrostatic potential $\phi$ [76], which also satisfies the Poisson equation. Similarly, the boundary conditions on $\psi^{(1)}_{n_{I_\alpha}}$ presented in Eq. 24 are for the direction(s) along which the system is extended. For the direction(s) along which the system is finite, zero Dirichlet boundary conditions need to be prescribed.
The key differences between the current and previous formulations [3, 85] for the dynamical matrix merits further elaboration. First and foremost, the current formulation is in the context of real-space DFT, making it applicable to systems of any dimensionality, whereas previous formulations have been in the context of planewave DFT — restricted to the use of periodic boundary conditions due to the Fourier basis — which can be inaccurate for lower dimensional systems, particularly those that are charged and/or have large dipole moments. In particular, we have carefully formulated the electrostatic and nonlocal pseudopotential contributions to the dynamical matrix so as to make them amenable to the real-space method, i.e., convergence to the desired level of accuracy does not require an unnecessarily fine grid. Second, at no additional computational cost, the formulation presented here provides the actual \( \psi_{n_{I_{\alpha}}}^{(1)} \) — quantity that can be directly used in physical applications — whereas previous formulations instead only ensure that \( \rho^{(1)}_{I_{\alpha}} \) and dynamical matrix \( \mathbf{D} \) are correctly computed, e.g., Refs. [3, 86] only determine the projection of \( \psi_{n_{I_{\alpha}}}^{(1)} \) onto the unoccupied space manifold, which keeps \( \rho^{(1)}_{I_{\alpha}} \) and \( \mathbf{D} \) unchanged. Finally, we provide the complete expressions and their derivation for the dynamical matrix and associated Sterneheimer equation, which have not been made available heretofore.

IV. IMPLEMENTATION AND RESULTS

We have implemented the aforementioned real-space formulation of DFPT for phonons in M-SPARC [87], which is a MATLAB version of the large-scale parallel C/C++ electronic structure code SPARC [68, 76, 77], both of which also employ the local formulation for the electrostatics adopted here. In M-SPARC/SPARC, all quantities are discretized on a uniform real-space grid, with high-order centered finite differences used for differential operators and the trapezoidal rule used for integral operators. The electronic ground state is determined using the self-consistent field (SCF) method [81], wherein partial diagonalization is performed in each iteration using the Chebyshev filtered subspace iteration (CheFSI) [88, 89], with self-consistency accelerated using the restarted Periodic Pulay mixing scheme [90, 91]. The Poisson equation for the electrostatic potential is solved using the alternating Anderson-Richardson (AAR) [92, 93] method.

The self-consistent solution of each Sterneheimer equation is determined using a fixed-point iteration with respect to \( \rho^{(1)}_{I_{\alpha}} \), accelerated using the restarted Periodic Pulay mixing scheme, with the non-interacting version of the system used as an initial guess, i.e., \( \rho^{(1)}_{I_{\alpha}} \) corresponding to the case when the electron density is assumed to be the superposition of isolated-atom electron densities. In each iteration of this self-consistent solution, the linear systems for \( \psi_{n_{I_{\alpha}}}^{(1)} \) and \( \phi_{I_{\alpha}}^{(1)} \) are solved using the conjugate gradient (CG) and AAR methods, respectively, with the incomplete Cholesky factorization of the discrete Laplacian matrix used as preconditioner, the boundary conditions enforced while performing stencil operations for the Laplacian matrix-vector products, and the solution obtained in the previous iteration used as the initial guess. To reduce the computer memory requirements, the dynamical matrix components are updated after the self-consistent solution of the Sterneheimer equation for each perturbation, thereby avoiding the need to store \( \psi_{n_{I_{\alpha}}}^{(1)} \). Due to numerical inaccuracies, since the computed interatomic force constants matrix does not satisfy the acoustic sum rule (ASR) — phonon frequencies of the acoustic modes must be zero, given the translational symmetry of the crystal — we enforce it by updating the diagonal components of the dynamical matrix so that the following conditions are satisfied:

\[
\sum_{J_{\alpha}} N \sqrt{M_{I_{\alpha}} M_{J_{\alpha}}} D_{I_{\alpha}, J_{\alpha}}(0, \mathbf{R}) = 0 \quad \forall \alpha \in \{1, 2, 3\}, \quad I \in \{1, 2, \ldots, N\}.
\] (29)

We now verify the accuracy of the developed formulation and implementation by comparisons with the established planewave code ABINIT [43, 86]. For this study, we consider three representative examples of various compositions, geometries, and dimensionalities, all at their equilibrium configurations: 1-atom primitive unit cell of body-centered cubic (BCC) cesium, with \( 8 \times 8 \times 8 \) Monkhorst-Pack [94] grid for Brillouin zone integration; 4-atom primitive unit cell of rectangular \( \alpha \)-phosphorene, with \( 8 \times 8 \) Monkhorst-Pack grid for Brillouin zone integration; and 2-atom primitive unit cell of the 1D carbon polymeric chain polyyne, with \( 11 \) Monkhorst-Pack grid points for Brillouin zone integration. In ABINIT, we use planewave cutoffs of 27, 35, and 120 Ha for the cesium, phosphorene, and polyyne systems, respectively, which translates to phonon frequencies converged to within 0.1 cm\(^{-1}\). In M-SPARC, we use a twelfth-order accurate finite-difference discretization with mesh sizes of 0.39, 0.25, and 0.12 bohr for the cesium, phosphorene, and polyyne systems, respectively, which translates to the phonon frequencies converged to within 1 cm\(^{-1}\). In all simulations, we employ optimized norm-conserving Vanderbilt (ONCV) pseudopotentials [95] from the SPMS set [96], Purdew-Zunger [97] variant of the local density approximation (LDA) [2] as the exchange-correlation functional, and Fermi-Dirac smearing of 0.001 Ha.
In Fig. 1, we present the phonon dispersion curves and the phonon density of states so obtained by M-SPARC and ABINIT for the chosen cesium, phospherene, and polyyne systems. In plotting the dispersion curves, we choose the high symmetry $\Gamma(0,0,0)$–$H(-0.5,0.5,0.5)$–$N(0,0,0.5)$–$\Gamma(0,0,0)$–$P(0.25,0.25,0.25)$–$N(0,0,0.5)$–$P(0.25,0.25,0.25)$–$H(-0.5,0.5,0.5)$ circuit for cesium; and high symmetry $\Gamma(0,0)$–$X(0.5,0)$–$S(0.5,0.5)$–$Y(0,0.5)$–$\Gamma(0,0)$–$S(0.5,0.5)$–$X(0.5,0)$–$Y(0,0.5)$ circuit for phospherene, the coordinates representing fractions of the lattice vectors. For the phonon density of states, we exclude the rigid body modes at the $q = 0$ phonon wavevector and smear the Dirac delta function using a Gaussian with widths of 2, 7, and 40 cm$^{-1}$ for the cesium, phospherene, and polyyne systems, respectively. It is clear from the results that there is excellent agreement between M-SPARC and ABINIT, with the maximum difference in phonon frequencies being 0.2, 0.93, and 0.61 cm$^{-1}$ for the cesium, phospherene, and polyyne systems, respectively. Indeed, the agreement between M-SPARC and ABINIT further increases on refining the real-space grid in M-SPARC.

Note that the phosphorene and polyyne systems do not have any dipole moment, hence the excellent agreement between the real-space and planewave formulations for the phonon spectrum. Indeed, for 2D and 1D systems, particularly those that are charged and/or have large dipole moments, the standard planewave formulations for phonons can lead to inaccurate results, because of the restriction of the Fourier basis to periodic boundary conditions. Also note that though the focus in the present work is on phonons, the developed DFPT framework is equally applicable to the calculation of vibrational spectra for isolated clusters/molecules, as shown in Appendix B. Overall, these results demonstrate the accuracy of the developed real-space formulation and implementation of DFPT for phonons.

V. CONCLUDING REMARKS

We have presented a real-space formulation and implementation of DFPT for the calculation of phonons. Specifically, employing a local form for the electrostatics, local exchange-correlation functional, and Kleinman-Bylander representation for nonlocal pseudopotentials, we have derived expressions for the dynamical matrix and associated Sternheimer equation at any arbitrary phonon wavevector in the framework of real-space Kohn-Sham DFT. The resulting formulation is applicable to insulating as well as metallic systems, irrespective of their dimensionality, for both orthogonal and non-orthogonal cells. We have also developed a high-order finite-difference implementation of the proposed formulation in the M-SPARC electronic structure code. We have verified the accuracy of the developed formulation and implementation by demonstrating excellent agreement with established planewave results for representative examples having different structure, composition, and dimensionality. Though the focus of the current work is phonons, the developed framework is equally applicable to the calculation of vibrational spectra for isolated systems/molecules.

The current work opens an avenue for the real-space formulation and implementation of DFPT for higher order derivatives, e.g., third-order interatomic force constants, and perturbations with respect to other quantities, e.g., electric fields. The development of a massively parallel implementation for DFPT in SPARC [68, 76, 77] — large-scale parallel C/C++ version of M-SPARC — will enable the study of responses to perturbations more efficiently and for larger systems, making it worthy of pursuit. In addition, the extension of DFPT to cyclic and helical symmetries [98, 99], which are encountered during the study of low dimensional materials and their response to mechanical deformations [100–102], is currently being pursued by the authors.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.
FIG. 1: Phonon dispersion and density of states for BCC cesium, \( \alpha \)-phospherene, and polyyne. The red (continuous) and the blue (dashed) curves in the dispersion plots represent the cubic spline fit to the data points obtained from ABINIT and M-SPARC, respectively. The maximum differences in the phonon frequencies between M-SPARC and ABINIT for the cesium, phospherene, and polyyne systems are 0.2, 0.93, and 0.61 cm\(^{-1}\), respectively.

**Author Declarations**

The authors have no conflicts to disclose.

**Appendix A: Real-space formulation of DFPT for phonons**

We now present the detailed real-space formulation and derivation for phonons, which has been summarized in Section III. The description for the quantities that are not defined here can be found in Sections II and III.
1. Atomic vibrations: matrix eigenproblem

Within the adiabatic harmonic approximation, the energy of the perturbed system can be expanded using a truncated Taylor series:

\[
E_{KS}(\mathbf{R} + \Delta \mathbf{R}) = E_{KS}(\mathbf{R}) - \sum_{I_{\alpha} = 1}^{3N} f_{I_{\alpha}}(\mathbf{R}) \Delta R_{I_{\alpha}} + \frac{1}{2} \sum_{I_{\alpha} = 1}^{3N} \sum_{J_{\beta} = 1}^{3N} \Delta R_{I_{\alpha}} \mathcal{C}_{I_{\alpha},J_{\beta}}(\mathbf{R}) \Delta R_{J_{\beta}},
\]

where \( \Delta \mathbf{R} = \{ \Delta \mathbf{R}_{1}, \Delta \mathbf{R}_{2}, \ldots, \Delta \mathbf{R}_{N} \} \) denotes the set of (small) atomic perturbations, \( f_{I_{\alpha}} \) is the force on the \( I^{th} \) atom in the \( \alpha \)th direction, and

\[
\mathcal{C}_{I_{\alpha},J_{\beta}}(\mathbf{R}) = \frac{\partial^2 E_{KS}(\mathbf{R})}{\partial R_{I_{\alpha}} \partial R_{J_{\beta}}}, \quad I, J = 1, 2, \ldots N, \quad \alpha, \beta = 1, 2, 3,
\]

is the second-order interatomic force constant matrix \( \mathbf{C} \). It follows from Eq. A1 that the atomic forces in the perturbed atomic configuration can be written as:

\[
f_{I_{\alpha}}(\mathbf{R} + \Delta \mathbf{R}) := -\frac{\partial E_{KS}(\mathbf{R} + \Delta \mathbf{R})}{\partial \Delta R_{I_{\alpha}}} = f_{I_{\alpha}}(\mathbf{R}) - \sum_{J_{\beta} = 1}^{3N} \mathcal{C}_{I_{\alpha},J_{\beta}}(\mathbf{R}) \Delta R_{J_{\beta}}.
\]

If the unperturbed system corresponds to an equilibrium atomic configuration, Newton’s second law of motion takes the form:

\[
M_{I} \frac{d^2 \Delta R_{I_{\alpha}}}{dt^2} = - \sum_{J_{\beta} = 1}^{3N} \mathcal{C}_{I_{\alpha},J_{\beta}}(\mathbf{R}) \Delta R_{J_{\beta}}.
\]

Assuming solutions of the form:

\[
\Delta R_{I_{\alpha}} = e^{i \omega t} v_{I_{\alpha}},
\]

where \( \omega \) and \( \mathbf{v} \) denote the frequency and mode of the lattice vibration, respectively, we arrive at the following generalized eigenproblem:

\[
\mathbf{C}(\mathbf{R}) \mathbf{v}(\mathbf{R}) = \omega^2(\mathbf{R})M(\mathbf{R})\mathbf{v}(\mathbf{R}),
\]

with \( \mathbf{M} \) being the mass matrix. To convert it to a standard eigenproblem, the following transformation is performed:

\[
\left( \mathbf{M}^{-1/2}(\mathbf{R}) \mathbf{C}(\mathbf{R}) \mathbf{M}^{-1/2}(\mathbf{R}) \right) \mathbf{M}^{1/2}(\mathbf{R}) \mathbf{v}(\mathbf{R}) = \omega^2(\mathbf{R}) \mathbf{M}^{-1/2}(\mathbf{R}) \mathbf{M}(\mathbf{R}) \mathbf{v}(\mathbf{R})
\Rightarrow \mathbf{D}(\mathbf{R}) \mathbf{u}(\mathbf{R}) = \omega^2(\mathbf{R}) \mathbf{u}(\mathbf{R}),
\]

where \( \mathbf{u} = \mathbf{M}^{1/2} \mathbf{v} \), and \( \mathbf{D} \) is referred to as the dynamical matrix, whose entries are given by:

\[
\mathcal{D}_{I_{\alpha},J_{\beta}}(\mathbf{R}) = \frac{1}{\sqrt{M_{I}M_{J}}} \frac{\partial^2 E_{KS}(\mathbf{R})}{\partial R_{I_{\alpha}} \partial R_{J_{\beta}}}, \quad I, J = 1, 2, \ldots N, \quad \alpha, \beta = 1, 2, 3.
\]

2. Block diagonalization of the dynamical matrix: phonon wavevector

The dynamical matrix \( \mathbf{D} \) is block-circulant, a consequence of the relation:

\[
\frac{\partial^2 E_{KS}(\mathbf{R})}{\partial R_{I_{\alpha}}^\alpha \partial R_{J_{\beta}}^\beta} = \frac{\partial^2 E_{KS}(\mathbf{R})}{\partial R_{I_{\alpha}}^{\beta-a} \partial R_{J_{\beta}}^{a}}, \quad I, J = 1, 2, \ldots \hat{N}, \quad \alpha, \beta = 1, 2, 3,
\]

whereby it can be block-diagonalized using the block-form of the discrete Fourier transform matrix. Therefore, the original eigenproblem (Eq. A7) can be reduced into a series of smaller eigenvalue problems:

\[
\tilde{\mathbf{D}}(\mathbf{R}, \mathbf{q}) \tilde{\mathbf{u}}(\mathbf{R}, \mathbf{q}) = \omega^2(\mathbf{R}, \mathbf{q}) \tilde{\mathbf{u}}(\mathbf{R}, \mathbf{q}),
\]
where $\tilde{D}$ is also referred to as the dynamical matrix — terminology chosen to be consistent with that adopted in literature [3] — that is indexed by the phonon wavevector $q = (q_1, q_2, q_3)$. In addition, $\omega$ and $\tilde{u}$ are the phonon frequencies and modes, respectively. The entries of $\tilde{D}$ take the form:

$$\tilde{D}_{Ia,I\beta}(R,q) = \frac{1}{\sqrt{M_I M_J}} \left[ \frac{1}{N_c} \sum_a \sum_b e^{i q (L_b - L_a)} \frac{\partial^2 E_{KS}(R)}{\partial R_{aI}^2 \partial R_{bJ}^2} \right], \quad I, J = 1, 2, \ldots N, \quad \alpha, \beta = 1, 2, 3. \quad (A11)$$

Here, $\omega$ and $\tilde{u}$ are the phonon frequencies and modes, respectively. In addition, we have the relation:

$$v^a_{Ia}(R,q) = \frac{1}{\sqrt{M_I N_c}} e^{i q L a} \tilde{u}^0_{Ia}(R,q), \quad (A12)$$

where we have introduced the phonon-wavevector dependence for $v$ to highlight its distinction from the eigenvectors of the eigenproblem in Eq. A6, as it has been stated. Note that the atomic perturbations corresponding to zero and non-zero phonon wavevectors $q$ are generally referred to as commensurate and incommensurate perturbations, respectively.

### 3. Dynamical matrix on $\Omega$

The expression for the dynamical matrix (Eq. A11) can be expanded as:

$$\tilde{D}_{Ia,J\beta}(R,q) = \frac{1}{\sqrt{M_I M_J}} \left[ \frac{1}{N_c} \sum_a \sum_b e^{i q (L_b - L_a)} \left( \frac{\partial^2 T_a(R)}{\partial R_{aI}^2 \partial R_{bJ}^2} + \frac{\partial^2 E_{xc}(R)}{\partial R_{aI}^2 \partial R_{bJ}^2} \right) + \frac{\partial^2 \psi_n(R,x)}{\partial R_{aI}^2 \partial R_{bJ}^2} \right] \cdot \quad (A13)$$

where we have used the decomposition of the Kohn-Sham energy into its various terms (Eq. 1). Below, we first derive real-space expressions for each of the contributions to the dynamical matrix appearing in the above equation, with all quantities/integrals defined over the cell $\Omega$. Then, we collect all terms to arrive at the complete expression for the dynamical matrix on $\Omega$.

#### a. Electronic kinetic energy contribution

The contribution to the dynamical matrix arising from the electronic kinetic energy:

$$\frac{\partial^2 T_a(R)}{\partial R_{aI}^2 \partial R_{bJ}^2} = \sum_{n=1}^{N_c} \left( \frac{\partial^2 T_a(R)}{\partial R_{aI}^2 \partial R_{bJ}^2} + \frac{\partial g_n(R)}{\partial R_{aI}^2} \left( \int_\Omega \frac{\partial^2 T_a(R)}{\partial R_{aI}^2} \frac{\partial \psi_n(R,x)}{\partial R_{bJ}^2} \right) dR \right) + \frac{\partial g_n(R)}{\partial R_{aI}^2} \left( \int_\Omega \frac{\partial^2 T_a(R)}{\partial R_{aI}^2} \frac{\partial \psi_n(R,x)}{\partial R_{bJ}^2} \right) dR$$

$$+ \frac{\partial g_n(R)}{\partial R_{bJ}^2} \left( \int_\Omega \frac{\partial^2 T_a(R)}{\partial R_{aI}^2} \frac{\partial \psi_n(R,x)}{\partial R_{bJ}^2} \right) dR$$

$$+ \frac{\partial^2 T_a(R)}{\partial R_{aI}^2} \frac{\partial ^2 \psi_n(R,x)}{\partial R_{bJ}^2} dR$$

$$= A_1(R) + A_2(R) + A_3(R) + A_4(R) + A_5(R), \quad (A14)$$

where

$$A_1(R) = - \sum_{n=1}^{N_c} \frac{\partial^2 g_n(R)}{\partial R_{aI}^2} \int_\Omega \psi_n(R,x) \nabla^2 \psi_n(R,x) dR,$$

$$A_2(R) = - \sum_{n=1}^{N_c} \frac{\partial g_n(R)}{\partial R_{aI}^2} \left( \int_\Omega \psi_n(R,x) \nabla^2 \psi_n(R,x) dR \right) + \int_\Omega \frac{\partial \psi_n(R,x)}{\partial R_{aI}^2} \nabla^2 \psi_n(R,x) dR.$$
b. Exchange-correlation energy contribution

The contribution to the dynamical matrix arising from the exchange-correlation energy:

\[
\frac{\partial^2 E_{xc}(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} = \int \frac{\delta^2 E_{xc}(\mathbf{R})}{\delta \rho(\mathbf{R}) \delta \rho(\mathbf{R})} \frac{\partial^2 \rho(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} \, dx + \int \frac{\partial \rho(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial^2 E_{xc}(\mathbf{R})}{\partial \rho(\mathbf{R}) \partial R_{jb}^b} \, dx,
\]

where

\[
B_1(\mathbf{R}) = 2 \sum_{n=1}^{N_e} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} \int \psi_n^*(\mathbf{R}) \mathbf{V}_{xc}(\rho(\mathbf{R})) \psi_n(\mathbf{R}) \, dx,
\]

\[
B_2(\mathbf{R}) = 2 \sum_{n=1}^{N_e} \left( \frac{\partial g_n(\mathbf{R})}{\partial R_{ia}^a} \int \psi_n^*(\mathbf{R}) \mathbf{V}_{xc}(\rho(\mathbf{R})) \frac{\partial \psi_n(\mathbf{R})}{\partial R_{ia}^a} \, dx + \int \frac{\partial \psi_n^*(\mathbf{R})}{\partial R_{ia}^a} \mathbf{V}_{xc}(\rho(\mathbf{R})) \psi_n(\mathbf{R}) \, dx \right),
\]

\[
B_3(\mathbf{R}) = 2 \sum_{n=1}^{N_e} \left( \frac{\partial g_n(\mathbf{R})}{\partial R_{jb}^b} \int \psi_n^*(\mathbf{R}) \mathbf{V}_{xc}(\rho(\mathbf{R})) \frac{\partial \psi_n(\mathbf{R})}{\partial R_{jb}^b} \, dx + \int \frac{\partial \psi_n^*(\mathbf{R})}{\partial R_{jb}^b} \mathbf{V}_{xc}(\rho(\mathbf{R})) \psi_n(\mathbf{R}) \, dx \right),
\]

\[
B_4(\mathbf{R}) = 2 \sum_{n=1}^{N_e} \left( \frac{\partial g_n(\mathbf{R})}{\partial R_{ia}^a} \int \psi_n^*(\mathbf{R}) \mathbf{V}_{xc}(\rho(\mathbf{R})) \frac{\partial \psi_n(\mathbf{R})}{\partial R_{ia}^a} \, dx + \frac{\partial^2 \rho(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} \mathbf{V}_{xc}(\rho(\mathbf{R})) \psi_n(\mathbf{R}) \, dx \right),
\]

\[
B_5(\mathbf{R}) = 2 \sum_{n=1}^{N_e} \left( \frac{\partial \rho(\mathbf{R})}{\partial R_{ia}^a} \left( 2 \frac{\partial^2 \mathbf{V}_{xc}(\rho(\mathbf{R}))}{\partial \rho(\mathbf{R})^2} \frac{\partial \psi_n(\mathbf{R})}{\partial R_{ia}^a} \right) \frac{\partial \rho(\mathbf{R})}{\partial R_{jb}^b} \, dx \right),
\]

\[
B_6(\mathbf{R}) = \int \frac{\partial \rho(\mathbf{R})}{\partial R_{ia}^a} \left( 2 \frac{\partial^2 \mathbf{V}_{xc}(\rho(\mathbf{R}))}{\partial \rho(\mathbf{R})^2} \frac{\partial \psi_n(\mathbf{R})}{\partial R_{ia}^a} \right) \frac{\partial \rho(\mathbf{R})}{\partial R_{jb}^b} \, dx.
\]

c. Electrostatic energy contribution

The contribution to the dynamical matrix arising from the electrostatic energy:

\[
\frac{\partial^2 E_{el}(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} = \int \frac{\delta^2 E_{el}(\mathbf{R})}{\delta \phi(\mathbf{R}) \delta \phi(\mathbf{R})} \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} \, dx
\]

\[
+ \int \frac{\delta E_{el}(\mathbf{R})}{\delta \phi(\mathbf{R})} \left( \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial \phi(\mathbf{R})}{\partial R_{jb}^b} + \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial \phi(\mathbf{R})}{\partial R_{jb}^b} \right) \, dx
\]

\[
+ \int \frac{\delta^2 E_{el}(\mathbf{R})}{\delta \phi(\mathbf{R})^2} \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{jb}^b} \, dx
\]

\[
+ \frac{1}{2} \int \left( \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} + \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \right) \, dx + \frac{1}{2} \int \left( \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} + \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \right) \, dx
\]

\[
+ \frac{1}{2} \int \left( \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} + \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \right) \, dx + \frac{1}{2} \int \left( \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} + \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \right) \, dx
\]

\[- 2 \delta_{ab} \delta_{ij} \left( \frac{1}{2} \int \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \, dx - \frac{1}{2} \int \frac{\partial \phi(\mathbf{R})}{\partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \, dx \right)
\]

\[- 2 \delta_{ab} \delta_{ij} \left( \frac{1}{2} \int \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \, dx - \frac{1}{2} \int \frac{\partial^2 \phi(\mathbf{R})}{\partial R_{ia}^a \partial R_{ia}^a} \frac{\partial V_{el}(\mathbf{R})}{\partial R_{jb}^b} \, dx \right)
\]
\begin{align}
C_1(\mathbf{R}) &= 2 \sum_{n=1}^{N_r} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{\alpha}^a \partial R_{\beta}^b} \int_{\Omega} \psi_n^*(\mathbf{x}, \mathbf{R}) \phi(\mathbf{x}, \mathbf{R}) \psi_n(\mathbf{x}, \mathbf{R}) \, d\mathbf{x},
C_2(\mathbf{R}) &= 2 \sum_{n=1}^{N_r} \frac{\partial g_n(\mathbf{R})}{\partial R_{\alpha}^a} \left( \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \phi(\mathbf{x}, \mathbf{R}) \right) \, d\mathbf{x} + \int_{\Omega} \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \phi(\mathbf{x}, \mathbf{R}) \psi_n(\mathbf{x}, \mathbf{R}) \, d\mathbf{x},
C_3(\mathbf{R}) &= 2 \sum_{n=1}^{N_r} \frac{\partial g_n(\mathbf{R})}{\partial R_{\beta}^b} \left( \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\beta}^b} \phi(\mathbf{x}, \mathbf{R}) \right) \, d\mathbf{x} + \int_{\Omega} \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\beta}^b} \phi(\mathbf{x}, \mathbf{R}) \psi_n(\mathbf{x}, \mathbf{R}) \, d\mathbf{x},
C_4(\mathbf{R}) &= 2 \sum_{n=1}^{N_r} g_n(\mathbf{R}) \left( \int_{\Omega} \psi_n^*(\mathbf{x}, \mathbf{R}) \phi(\mathbf{x}, \mathbf{R}) \frac{\partial^2 \psi_n(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a \partial R_{\beta}^b} \, d\mathbf{x} + \int_{\Omega} \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \phi(\mathbf{x}, \mathbf{R}) \psi_n(\mathbf{x}, \mathbf{R}) \, d\mathbf{x} \right),
C_5(\mathbf{R}) &= 2 \sum_{n=1}^{N_r} g_n(\mathbf{R}) \left( \int_{\Omega} \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \phi(\mathbf{x}, \mathbf{R}) \frac{\partial \psi_n(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \, d\mathbf{x} + \int_{\Omega} \frac{\partial \psi_n^*(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \phi(\mathbf{x}, \mathbf{R}) \psi_n(\mathbf{x}, \mathbf{R}) \, d\mathbf{x} \right),
C_6(\mathbf{R}) &= \int_{\Omega} \frac{\partial^2 b(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a \partial R_{\beta}^b} \phi(\mathbf{x}, \mathbf{R}) \, d\mathbf{x} = \delta_{ab} \delta_{IJ} \int_{\Omega} \nabla_\alpha \nabla_\beta b_J(\mathbf{x}, R_b^J) \phi(\mathbf{x}, \mathbf{R}) \, d\mathbf{x},
C_7(\mathbf{R}) &= \frac{1}{2} \int_{\Omega} \left( \frac{\partial (\rho(\mathbf{x}, \mathbf{R}) + b(\mathbf{x}, \mathbf{R}))}{\partial R_{\alpha}^a} \frac{\partial \phi(\mathbf{x}, \mathbf{R})}{\partial R_{\beta}^b} + \frac{\partial (\rho(\mathbf{x}, \mathbf{R}) + b(\mathbf{x}, \mathbf{R}))}{\partial R_{\beta}^b} \frac{\partial \phi(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \right) \, d\mathbf{x},
C_8(\mathbf{R}) &= \frac{1}{2} \int_{\Omega} \left( \nabla_\alpha b_J(\mathbf{x}, R_b^J) + \nabla_\alpha b_J(\mathbf{x}, R_b^J) \right) \left( \nabla_\beta \tilde{V}_J(\mathbf{x}, R_b^J) - \nabla_\beta V_J(\mathbf{x}, R_b^J) \right) \, d\mathbf{x} + \frac{1}{2} \int_{\Omega} \left( \nabla_\beta b_J(\mathbf{x}, R_b^J) + \nabla_\beta \tilde{b}_J(\mathbf{x}, R_b^J) \right) \left( \nabla_\alpha \tilde{V}_J(\mathbf{x}, R_b^J) - \nabla_\alpha V_J(\mathbf{x}, R_b^J) \right) \, d\mathbf{x},
\end{align}

where

\begin{equation}
= C_1(\mathbf{R}) + C_2(\mathbf{R}) + C_3(\mathbf{R}) + C_4(\mathbf{R}) + C_5(\mathbf{R}) + C_6(\mathbf{R}) + C_7(\mathbf{R}) + C_8(\mathbf{R}),
\end{equation}

In obtaining the above relations, we have used integration by parts, the spherical symmetry of the pseudocharge densities and potentials, and the fact that the ground state electrostatic potential satisfies the Poisson equation (Eq. 10).

d. Nonlocal pseudopotential energy contribution

The contribution to the dynamical matrix arising from the nonlocal pseudopotential energy:

\begin{align}
\frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\alpha}^a \partial R_{\beta}^b} &= \sum_{n=1}^{N_r} \left( \frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\alpha}^a} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{\beta}^b} + \sum_{J=1}^{N_p} \sum_{p=1}^{N_p} \right) \left( \frac{\partial g_n(\mathbf{R})}{\partial R_{\alpha}^a} \frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\beta}^b} \delta_{\chi_J(p)(\mathbf{x}, \mathbf{R})} \right) \, d\mathbf{x} + \int_{\Omega} \frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\alpha}^a} \frac{\partial \chi_J(p)(\mathbf{x}, \mathbf{R})}{\partial R_{\beta}^b} \, d\mathbf{x} + \int_{\Omega} \frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\beta}^b} \frac{\partial \chi_J(p)(\mathbf{x}, \mathbf{R})}{\partial R_{\alpha}^a} \, d\mathbf{x} + \int_{\Omega} \delta_{\chi_J(p)(\mathbf{x}, \mathbf{R})} \frac{\partial^2 E_{nl}(\mathbf{R})}{\partial R_{\alpha}^a} \delta_{\chi_J(p)(\mathbf{x}, \mathbf{R})} \, d\mathbf{x}
\end{align}
where

\[ D_1(R) = 2 \sum_{n=1}^{N} \frac{\partial^2 g_n(R)}{\partial R^a_n \partial R^b_j} \int_\Omega \int \psi^*_n(x, R) V_{nl}(x, x', R) \psi_n(x', R) \, dx \, dx' \]

\[ D_2(R) = 2 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R^a_n} \left( \int_\Omega \int \psi^*_n(x, R) V_{nl}(x, x', R) \frac{\partial \psi_n(x', R)}{\partial R^b_j} \, dx \, dx' \right) \]

\[ D_3(R) = 2 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R^b_j} \left( \int_\Omega \int \psi^*_n(x, R) V_{nl}(x, x', R) \frac{\partial \psi_n(x', R)}{\partial R^a_n} \, dx \, dx' \right) \]

\[ D_4(R) = 2 \sum_{n=1}^{N} g_n(R) \left( \int_\Omega \int \psi^*_n(x, R) V_{nl}(x, x', R) \frac{\partial^2 \psi_n(x', R)}{\partial R^a_n \partial R^b_j} \, dx \, dx' \right) \]

\[ D_5(R) = 2 \sum_{n=1}^{N} g_n(R) \left( \int_\Omega \int \frac{\partial^2 \psi^*_n(x, R)}{\partial R^a_n \partial R^b_j} V_{nl}(x, x', R) \frac{\partial \psi_n(x', R)}{\partial R^a_n} \, dx \, dx' \right) \]

\[ D_6(R) = 2 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R^a_n} \sum_{p=1}^{P} \gamma_{jp} \left( \int_\Omega \psi^*_n(x, R) \frac{\partial \chi_{jp}(x, R^b_j)}{\partial R^b_j} \, dx \right) \int_\Omega \chi_{jp}(x, R^b_j) \psi_n(x, R) \, dx \]

\[ + \int_\Omega \psi^*_n(x, R) \chi_{jp}(x, R^b_j) \, dx \int_\Omega \frac{\partial \psi^*_n(x, R)}{\partial R^b_j} \psi_n(x, R) \, dx \]

\[ = -4 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R^a_n} \sum_{p=1}^{P} \gamma_{jp} R \left( \int_\Omega \psi^*_n(x, R) \nabla_\beta \chi_{jp}(x, R^b_j) \, dx \right) \int_\Omega \chi_{jp}(x, R^b_j) \psi_n(x, R) \, dx \]
\[ D_7(R) = 2 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R_{j\beta}^n} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \frac{\partial \chi_{J,p}(x, R^a_j)}{\partial R_{j\alpha}^a} \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{I,p}(x, R^a_j) \ dx \int_{\Omega} \frac{\partial \chi_{J,p}(x, R^a_j)}{\partial R_{j\alpha}^a} \psi_n(x, R) \ dx \right) \\
= -4 \sum_{n=1}^{N} \frac{\partial g_n(R)}{\partial R_{j\beta}^n} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \nabla_\alpha \chi_{I,p}(x, R^a_j) \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
D_8(R) = 2 \sum_{n=1}^{N} g_n(R) \delta_{ab} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \frac{\partial^2 \chi_{J,p}(x, R^b_j)}{\partial R_{j\alpha}^a \partial R_{j\beta}^b} \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \frac{\partial^2 \chi_{I,p}(x, R^b_j)}{\partial R_{j\alpha}^a \partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
= 4 \sum_{n=1}^{N} g_n(R) \delta_{ab} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \nabla_\alpha \nabla_\beta \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
D_9(R) = 2 \sum_{n=1}^{N} g_n(R) \delta_{ab} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \frac{\partial \chi_{J,p}(x, R^b_j)}{\partial R_{j\alpha}^a} \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^a_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^a_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
= 4 \sum_{n=1}^{N} g_n(R) \delta_{ab} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \nabla_\alpha \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \nabla_\alpha \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
D_{10}(R) = 2 \sum_{n=1}^{N} g_n(R) \delta_{ab} \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \frac{\partial \chi_{J,p}(x, R^a_j)}{\partial R_{j\alpha}^a} \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^b_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^a_j) \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^b_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
= -2 \sum_{n=1}^{N} g_n(R) \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \nabla_\alpha \chi_{J,p}(x, R^a_j) \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \frac{\partial \psi_n(x, R)}{\partial R_{j\beta}^a} \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^a_j) \ dx \int_{\Omega} \nabla_\alpha \chi_{I,p}(x, R^a_j) \psi_n(x, R) \ dx \right) \\
D_{11}(R) = 2 \sum_{n=1}^{N} g_n(R) \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^a_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \frac{\partial \chi_{I,p}(x, R^a_j)}{\partial R_{j\beta}^b} \psi_n(x, R) \ dx \right) \\
= -2 \sum_{n=1}^{N} g_n(R) \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \nabla_\alpha \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \chi_{I,p}(x, R^a_j) \frac{\partial \psi_n(x, R)}{\partial R_{j\beta}^b} \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \nabla_\beta \chi_{J,p}(x, R^b_j) \ dx \int_{\Omega} \chi_{I,p}(x, R^b_j) \frac{\partial \psi_n(x, R)}{\partial R_{j\alpha}^b} \ dx \right) \\
D_{12}(R) = 2 \sum_{n=1}^{N} g_n(R) \sum_{p=1}^{P_1} \gamma_{j,p} \left( \int_{\Omega} \psi_n^s(x, R) \chi_{I,p}(x, R^a_j) \ dx \int_{\Omega} \frac{\partial \chi_{J,p}(x, R^a_j)}{\partial R_{j\alpha}^a} \psi_n(x, R) \ dx \right) \\
+ \int_{\Omega} \psi_n^s(x, R) \chi_{I,p}(x, R^a_j) \ dx \int_{\Omega} \frac{\partial \chi_{J,p}(x, R^a_j)}{\partial R_{j\alpha}^a} \psi_n(x, R) \ dx \right)
\[ \chi \]

Next, we use the following relations:

The contribution to the dynamical matrix arising from the electronic entropy energy:

\[ \frac{\partial^2 E_{\text{ent}}(\mathbf{R})}{\partial R_{1a}^a \partial R_{1b}^b} = \sum_{n=1}^{N_z} \frac{\delta^2 E_{\text{ent}}(\mathbf{R})}{\delta g_n^a(\mathbf{R}) \delta g_n^b(\mathbf{R})} \left( \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{1a}^a} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{1b}^b} + \frac{\partial^2 E_{\text{ent}}(\mathbf{R})}{\delta g_n(\mathbf{R})^2} \right) \]

where

\[ E_1(\mathbf{R}) = 2k_B T \sum_{n=1}^{N_z} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{1a}^a} \log \left( \frac{g_n(\mathbf{R})}{1 - g_n(\mathbf{R})} \right) , \]

\[ E_2(\mathbf{R}) = 2k_B T \sum_{n=1}^{N_z} \frac{\partial g_n(\mathbf{R})}{\partial R_{1a}^a} \frac{\partial g_n(\mathbf{R})}{\partial R_{1b}^b} \frac{1}{g_n(\mathbf{R})(1 - g_n(\mathbf{R}))} . \]

f. Complete dynamical matrix Collecting all the contributions obtained above, the dynamical matrix take the form:

\[ \tilde{D}_{1a,1b}(\mathbf{R}, \mathbf{q}) = \frac{1}{\sqrt{M_1 M_2}} \left[ \frac{1}{N_c} \sum_a \sum_b e^{i(\mathbf{L}_a - \mathbf{L}_b)} \left( A_1(\mathbf{R}) + A_2(\mathbf{R}) + A_3(\mathbf{R}) + A_4(\mathbf{R}) + A_5(\mathbf{R}) \right. \right. \]

Next, we use the following relations:

\[ A_1(\mathbf{R}) + B_1(\mathbf{R}) + C_1(\mathbf{R}) + D_1(\mathbf{R}) + E_1(\mathbf{R}) = \lambda_f(\mathbf{R}) \left( \sum_{n=1}^{N_z} \frac{\partial^2 g_n(\mathbf{R})}{\partial R_{1a}^a} \frac{\partial g_n(\mathbf{R})}{\partial R_{1b}^b} \right) = 0 , \]

\[ A_2(\mathbf{R}) + B_2(\mathbf{R}) + C_2(\mathbf{R}) + D_2(\mathbf{R}) = 0 , \]
\[ A_3(R) + B_3(R) + C_3(R) + D_3(R) = 0, \]
\[ A_4(R) + B_4(R) + C_4(R) + D_4(R) = -2 \sum_{n=1}^{N_s} g_n(R) \lambda_n(R) \left( \int_{\Omega} \frac{\partial \psi_n^*(x, R)}{\partial R_i^a} \frac{\partial \psi_n(x, R)}{\partial R_j^b} \, dx \right), \]
where the first equality is obtained using Eqs. 8 and 9, and the second, third and fourth equalities are a consequence of Eq. 8 and the normalization condition on the Kohn-Sham orbitals.

Introducing the notation:
\[ \rho_{I_\alpha}^{(1)}(x, R, q) := \sum_a e^{iq \cdot L_a} \frac{\partial \rho(x, R)}{\partial R_i^a}, \]
\[ b_{I_\alpha}^{(1)}(x, R, q) := \sum_a e^{iq \cdot L_a} \frac{\partial b(x, R)}{\partial R_i^a}, \]
\[ \phi_{I_\alpha}^{(1)}(x, R, q) := \sum_a e^{iq \cdot L_a} \frac{\partial \phi(x, R)}{\partial R_i^a}, \]
\[ \psi_{I_\alpha}^{(1)}(x, R, q) := \sum_a e^{iq \cdot L_a} \frac{\partial \psi_n(x, R)}{\partial R_i^a}, \]
\[ g_{I_\alpha}^{(1)}(R, q) := \sum_a e^{iq \cdot L_a} \frac{\partial g_n(R)}{\partial R_i^a}, \]
the dynamical matrix takes the form:
\[ \tilde{D}_{I_\alpha, J_\beta}(R, q) = \frac{1}{\sqrt{M_I M_J}} \left[ \tilde{D}_\text{var}^{I_\alpha, J_\beta}(R, q) + \tilde{D}_\text{exc}^{I_\alpha, J_\beta}(R, q) + \tilde{D}_\text{elec}^{I_\alpha, J_\beta}(R, q) + \tilde{D}_\text{ent}^{I_\alpha, J_\beta}(R, q) + \tilde{D}_\text{ext}^{I_\alpha, J_\beta}(R, q) \right], \]
where the variational contribution to the dynamical matrix:
\[ \tilde{D}_\text{var}^{I_\alpha, J_\beta}(R, q) = \frac{1}{N_c} \sum_a \sum_b e^{iq \cdot (L_b - L_a)} \left( A'_4(R) + B'_4(R) + C'_4(R) + D'_4(R) + A'_5(R) + B'_5(R) + C'_5(R) + D'_5(R) \right) \]
\[ = \frac{1}{N_c} \sum_{n=1}^{N_s} g_n(R) \left( \int_{\Omega} \psi_{I_\alpha}^{(1)}(x, R, q) (H(R) - \lambda_n(R)) \psi_{I_\alpha}^{(1)}(x, R, q) \, dx + \int_{\Omega} \psi_{J_\beta}^{(1)}(x, R, -q) \right) \]
\[ \times (H(R) - \lambda_n(R)) \psi_{J_\beta}^{(1)}(x, R, -q) \, dx \right), \]
the exchange-correlation contribution to the dynamical matrix:
\[ \tilde{D}_\text{exc}^{I_\alpha, J_\beta}(R, q) = \frac{1}{N_c} \sum_a \sum_b e^{iq \cdot (L_b - L_a)} B_0(R) \]
\[ = \frac{1}{N_c} \int_{\Omega} \rho_{I_\alpha}^{(1)*}(x, R, q) \left( 2 \frac{\partial \epsilon_{xc}(\rho(x, R))}{\partial \rho(x, R)} + \rho(x, R) \frac{\partial^2 \epsilon_{xc}(\rho(x, R))}{\partial \rho^2(x, R)} \right) \rho_{J_\beta}^{(1)}(x, R, q) \, dx, \]
the electrostatics contribution to the dynamical matrix:
\[ \tilde{D}_\text{elec}^{I_\alpha, J_\beta}(R, q) = \frac{1}{N_c} \sum_a \sum_b e^{iq \cdot (L_b - L_a)} \left( C_6(R) + C_7(R) + C_8(R) \right) \]
\[ = \frac{1}{2N_c} \left( \int_{\Omega} \nabla_a \nabla_b b_f(x, R^a_j) \phi(x, R) \, dx + \int_{\Omega} \left( \rho_{I_\alpha}^{(1)*}(x, R, q) + b_{I_\alpha}^{(1)*}(x, R, q) \right) \phi_{J_\beta}^{(1)}(x, R, q) \, dx \right) \]
\[ + \int_{\Omega} \phi_{I_\alpha}^{(1)*}(x, R, q) \left( \rho_{J_\beta}^{(1)}(x, R, q) + b_{J_\beta}^{(1)}(x, R, q) \right) \, dx + \int_{\Omega} \sum_a e^{-iqL_a} \left( \nabla_a b_f(x, R^a_j) + \nabla_a b_f(x, R^j_a) \right) \]
the nonlocal pseudopotential contribution to the dynamical matrix:

$$\hat{c}^{nl}_{I_a}J_{b}(R, q) = \frac{1}{N_c} \sum_{a} e^{i q \cdot L_a} \left( \sum_{b} e^{i q \cdot L_b} \left( D_0(R) + D_7(R) + D_8(R) + D_9(R) + D_{10}(R) + D_{11}(R) + D_{12}(R) + D_{13}(R) \right) \right) \times \mathfrak{R} \left( \int_{\Omega} \psi_{n}^{*}(x, R) \nabla_{\beta} \chi_{J,p}(x, R_{j}^{b}) dx \int_{\Omega} \chi_{J,p}(x, R_{j}^{b}) \psi_{n}(x, R) dx \right)$$

$$+ \sum_{a} e^{-i q \cdot L_a} \left( \int_{\Omega} \psi_{n}^{*}(x, R) \nabla_{\alpha} \hat{V}_{J}(x, R_{j}^{a}) dx \int_{\Omega} \chi_{J,p}(x, R_{j}^{b}) \psi_{n}(x, R) dx \right)$$

$$- \delta_{IJ} \sum_{b} \int_{\Omega} \nabla_{\alpha} \tilde{b}_{J}(x, R_{j}^{b}) \nabla_{\beta} \hat{V}_{J}(x, R_{j}^{b}) dx - \delta_{IJ} \sum_{b} \int_{\Omega} \nabla_{\beta} \tilde{b}_{J}(x, R_{j}^{b}) \nabla_{\alpha} \hat{V}_{J}(x, R_{j}^{b}) dx$$

$$- \delta_{IJ} \sum_{b} \int_{\Omega} \nabla_{\alpha} \nabla_{\beta} \tilde{b}_{J}(x, R_{j}^{b}) \hat{V}_{J}(x, R_{j}^{b}) dx - \delta_{IJ} \sum_{b} \int_{\Omega} \hat{b}_{J}(x, R_{j}^{b}) \nabla_{\alpha} \nabla_{\beta} \hat{V}_{J}(x, R_{j}^{b}) dx \right), \quad \text{(A32)}$$

\( \hat{c}^{nl}_{I_a}J_{b}(R, q) \)
and the entropic contribution to the dynamical matrix:

\[
\tilde{c}_\alpha^{ent}(R, q) = \frac{1}{Nc} \sum_a \sum_b e^{iq(\mathbf{L}_b - \mathbf{L}_a)} E_2(R) \\
= \frac{1}{Nc} 2k_B T \sum_{n=1}^{N_c} g_n^{(1)}(R, q) g_n^{(1)}(R, q) \left( \frac{1}{g_n(R)} \frac{1}{g_n(R)} \right). \tag{A34}
\]

4. Boundary conditions on \( \hat{\Omega} \)

We now present the boundary conditions for \( \rho^{(1)}_{\alpha}, b^{(1)}_{\alpha}, \phi^{(1)}_{\alpha}, \) and \( \psi^{(1)}_{\alpha} \) on the unit cell/fundamental domain \( \hat{\Omega} \).

a. Electron density  The boundary conditions for \( \rho^{(1)}_{\alpha} \) on \( \Omega \) can be stated as:

\[
\rho^{(1)}_{\alpha}(x + L_j, R, q) = e^{iqL_j} \rho^{(1)}_{\alpha}(x, R, q), \quad j = 1, 2, 3, \tag{A35}
\]

which follow from the relation:

\[
\rho^{(1)}_{\alpha}(x + L_b, R, q) = \sum_a e^{iqL_a} \frac{\partial \rho(x + L_b, R)}{\partial R^{a}_{\alpha}} \\
= e^{iqL_b} \sum_a e^{iqL_a} \frac{\partial \rho(x, R)}{\partial R^{a}_{\alpha}} \\
= e^{iqL_b} \rho^{(1)}_{\alpha}(x, R, q), \tag{A36}
\]

where we have used the translational invariance of the lattice, and the periodic nature of the electron density:

\[
\rho(x + L_b, R) = \rho(x, R). \tag{A37}
\]

b. Pseudocharge density  The boundary conditions for \( b^{(1)}_{\alpha} \) on \( \hat{\Omega} \) can be stated as:

\[
b^{(1)}_{\alpha}(x + L_j, R, q) = e^{iqL_j} b^{(1)}_{\alpha}(x, R, q), \quad j = 1, 2, 3, \tag{A38}
\]

which follow from the relation:

\[
b^{(1)}_{\alpha}(x + L_b, R, q) = \sum_a e^{iqL_a} \frac{\partial b(x + L_b, R)}{\partial R^{a}_{\alpha}} \\
= -\sum_a e^{iqL_a} \nabla_a b_j(x + L_b, R^a) \\
= -e^{iqL_b} \sum_a e^{iqL_a} \nabla_a b_j(x, R^a) \\
= e^{iqL_b} b^{(1)}_{\alpha}(x, R, q), \tag{A39}
\]

where we have used the spherical symmetry of each atom’s pseudocharge density, translational invariance of the lattice, and the periodic nature of the pseudocharge density:

\[
b(x + L_b, R) = b(x, R). \tag{A40}
\]

c. Electrostatic potential  The boundary conditions on \( \phi^{(1)}_{\alpha} \) (Eq. 22) follow from the relation:

\[
\phi^{(1)}_{\alpha}(x + L_b, R, q) = \sum_a e^{iqL_a} \frac{\partial \phi(x + L_b, R)}{\partial R^{a}_{\alpha}} \\
= e^{iqL_b} \sum_a e^{iqL_a} \frac{\partial \phi(x, R)}{\partial R^{a}_{\alpha}} \\
= e^{iqL_b} \phi^{(1)}_{\alpha}(x, R, q), \tag{A41}
\]

where we have used the translational invariance of the lattice, and the periodic nature of the electrostatic potential:

\[
\phi(x + L_b, R) = \phi(x, R). \tag{A42}
\]
d. Orbitals  The boundary conditions on $\psi_{nI_\alpha}^{(1)}$ (Eq. 24) follow from the relation:

$$
\psi_{nI_\alpha}^{(1)}(x + L_b, R, k, q) = \sum_a e^{i^{a\cdot qL_a}} \frac{\partial \psi_n(x + L_b, R, k)}{\partial R_{I_\alpha}^a} \\
= e^{i^{(k+q)\cdot L_b}} \sum_a e^{i^{a\cdot qL_a-b}} \frac{\partial \psi_n(x, R, k)}{\partial R_{I_\alpha}^{a-b}} \\
= e^{i^{(k+q)\cdot L_b}} \psi_{nI_\alpha}^{(1)}(x, R, k, q),
$$

(A43)

where we have used the translational invariance of the lattice, and the Bloch-periodic nature of the Kohn-Sham orbitals:

$$
\psi_n(x + L_b, R, k) = e^{i^{k\cdot L_b}} \psi_n(x, R, k).
$$

(A44)

Note that we have introduced the dependence on the wavevector $k$ to signify that the orbitals can be indexed by $k$, given the translational symmetry present in the crystal. Also note that, consistent with implementations of DFT, we assume that the orbitals now satisfy the normalization constraint on $\hat{\Omega}$, rather than $\Omega$.

5. Sternheimer equation

We now derive the Sternheimer equation [84] for $\psi_{nI_\alpha}^{(1)}$ on the unit cell/fundamental domain $\hat{\Omega}$. As part of this formulation, we also need to derive the equations for $g_{nI_\alpha}$ and $\phi_{nI_\alpha}^{(1)}$, which we do first.

a. Occupations  The equation for $g_{nI_\alpha}$ can be obtained by applying $\sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a}$ on the Fermi-Dirac distribution for the occupations (Eq. 9):

$$
\sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a} (g_n(R, k)) = \left(1 + \exp \left(\frac{\lambda_n(R, k) - \lambda_f(R)}{k_B T}\right)\right)^{-1}.
$$

(A45)

In particular,

$$
\sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a} (g_n(R, k)) = g_{nI_\alpha}^{(1)}(R, k, q),
$$

(A46)

and

$$
\sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a} \left(\left(1 + \exp \left(\frac{\lambda_n(R, k) - \lambda_f(R)}{k_B T}\right)\right)^{-1}\right) = -\frac{g_n(R, k)(1 - g_n(R, k))}{k_B T} \sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a} \left(1 + \exp \left(\frac{\lambda_n(R, k) - \lambda_f(R)}{k_B T}\right)\right) \\
= -\frac{g_n(R, k)(1 - g_n(R, k))}{k_B T} \left(\lambda_{nI_\alpha}^{(1)}(R, k, q) - \lambda_{F_{nI_\alpha}}^{(1)}(R, q)\right),
$$

(A47)

where

$$
\lambda_{nI_\alpha}^{(1)}(R, k, q) = \delta_{q0} \int_{\hat{\Omega}} \psi_n^*(x, R, k) \psi_{nI_\alpha}^{(1)}(R, k, q) \psi_n(x, R, k) \, dx,
$$

(A48)

$$
\lambda_{F_{nI_\alpha}}^{(1)}(R, q) = \frac{\int_{\Omega} \sum_{n=1}^{N_{\alpha}(k)} g_n(R, k)(1 - g_n(R, k)) \lambda_{nI_\alpha}^{(1)}(R, k, q) \, dk}{\int_{\Omega} \sum_{n=1}^{N_{\alpha}(k)} g_n(R, k)(1 - g_n(R, k)) \, dk},
$$

(A49)

with the expression for $\lambda_{nI_\alpha}^{(1)}(R, k, q)$ derived in Eqn. A61, and the expression for $\lambda_{F_{nI_\alpha}}^{(1)}(R, q)$ obtained by applying $\sum_a e^{i^{qs\cdot L_a}} \frac{\partial}{\partial R_{I_\alpha}^a}$ on the constraint for the number of electrons (Eq. 9). In so doing, the constraint on the number of electrons in $\Omega$ has been rewritten as the constraint on the number of electrons on $\hat{\Omega}$.
b. Electrostatic potential  The equation for $\phi^{(1)}_{I_a}$ can be obtained by applying $\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}}$ on the Poisson equation for the electrostatics (Eq. 10):

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( -\frac{1}{4\pi} \nabla^2 \phi(x, R) = \rho(x, R) + b(x, R) \right).$$  \hspace{1cm} (A50)

In particular,

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( -\frac{1}{4\pi} \nabla^2 \phi(x, R) \right) = -\frac{1}{4\pi} \nabla^2 \sum_a e^{iq_{I_a}}(R, q)\phi(x, R) = -\frac{1}{4\pi} \nabla^2 \phi^{(1)}_{I_a}(x, R, q),$$  \hspace{1cm} (A51)

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} (\rho(x, R)) = \rho^{(1)}_{I_a}(x, R, q),$$  \hspace{1cm} (A52)

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} (b(x, R)) = b^{(1)}_{I_a}(x, R, q),$$  \hspace{1cm} (A53)

where the expressions for $\rho^{(1)}_{I_a}$ and $b^{(1)}_{I_a}$ can be found in Eqns. 17 and 19, respectively.

c. Orbitals  The Sternheimer equation for $\psi^{(1)}_{I_a}$ can be obtained by applying $\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}}$ on the Kohn-Sham eigenproblem (Eq. 8):

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( \mathcal{H}(R)\psi_n(x, R, k) = \lambda_n(R, k)\psi_n(x, R, k) \right)$$  \hspace{1cm} (A54)

where we have used dependence on wavevector $k$ to signify that it can be used to label the relevant quantities, a consequence of the translational symmetry in the system. Note that we are still considering the above equation on $\Omega$. In particular, the terms on the left hand side of Eq. A54 are transformed as follows:

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( \frac{1}{2} \nabla^2 \psi_n(x, R, k) \right) = \frac{1}{2} \nabla^2 \sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \psi_n(x, R, k) = \frac{1}{2} \nabla^2 \psi^{(1)}_{I_a}(x, R, k, q),$$  \hspace{1cm} (A55)

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( V_{xc}(\rho(R))\psi_n(x, R, k) \right) = \frac{\partial V_{xc}(\rho(R))}{\partial \rho(R)} \sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \psi_n(x, R, k) + V_{xc}(\rho(R)) \sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \psi_n(x, R, k) = \frac{\partial V_{xc}(\rho(R))}{\partial \rho(R)} \psi^{(1)}_{I_a}(x, R, k, q) + V_{xc}(\rho(R)) \psi^{(1)}_{I_a}(x, R, k, q),$$  \hspace{1cm} (A56)

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( \phi(R)\psi_n(x, R, k) \right) = \sum_a e^{iq_{I_a}} \phi(R)\psi_n(x, R, k) + \phi(R) \sum_a e^{iq_{I_a}} \psi_n(x, R, k) = \phi^{(1)}_{I_a}(R, k, q) \psi_n(x, R, k) + \phi(R) \psi^{(1)}_{I_a}(x, R, k, q),$$  \hspace{1cm} (A57)

with the nonlocal pseudopotential term transformed as follows:

$$\sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \left( V_{nl}(R)\psi_n(x, R, k) \right)$$

$$= \sum_a e^{iq_{I_a}} \frac{\partial}{\partial R^a_{I_a}} \sum_{l=1}^N \sum_{b=1}^P \gamma_{l,b} e^{iK_{l,b}} \chi_{I_a}^\ast \int_{\Omega} \chi_{I_a}^\ast \psi_n(x, R, k) \psi_n(x, R, k) dx$$

$$= -\sum_a e^{iq_{I_a}} \sum_{p=1}^P \gamma_{l,b} e^{iK_{l,b}} \nabla_\alpha \chi_{I_a}^\ast \int_{\Omega} \chi_{I_a}^\ast \psi_n(x, R, k) \psi_n(x, R, k) dx$$

$$- \sum_a e^{iq_{I_a}} \sum_{p=1}^P \gamma_{l,b} e^{iK_{l,b}} \chi_{I_a} \int_{\Omega} \nabla_\alpha \chi_{I_a} \psi_n(x, R, k) \psi_n(x, R, k) dx$$

$$+ \sum_{l=1}^N \sum_{b=1}^P \gamma_{l,b} e^{iK_{l,b}} \int_{\Omega} \chi_{I_a} \psi_n(x, R, k) \psi_n(x, R, k) dx$$
\[
= - \sum_{p=1}^{P_I} \sum_{a} e^{i(k+q) \cdot L_a} \nabla_{a} \chi_{I,p}(x, R_I^a) \sum_{b} \int_{\Omega} \chi_{I,p}^*(x, R_I^{a-b}) e^{-ik \cdot L_{a-b}} \psi_n(x, R, k) \, dx
- \sum_{p=1}^{P_I} \sum_{a} e^{i(k+q) \cdot L_a} \chi_{I,p}(x, R_I^a) \sum_{b} \int_{\Omega} \nabla_{a} \chi_{I,p}^*(x, R_I^{a-b}) e^{-ik \cdot L_{a-b}} \psi_n(x, R, k) \, dx
+ \sum_{l=1}^{N} \sum_{b} \sum_{p=1}^{P_I} e^{i(k+q) \cdot L_b} \chi_{I,p}(x, R_I^b) \sum_{c} \int_{\Omega} \chi_{I,p}^*(x, R_I^{b-c}) e^{-ik \cdot L_a} e^{i(k+q) \cdot L_a} \psi_n(x, R, k) \, dx
\]

and the right hand side of Eq. A54 is transformed as follows:

\[
\begin{aligned}
\sum_{a} e^{iq \cdot L_a} \frac{\partial}{\partial R_I^{a}} \left( \lambda_n(R, k) \psi_n(x, R, k) \right) &= \sum_{a} e^{iq \cdot L_a} \lambda_n(R, k) \psi_n(x, R, k) + \lambda_n(R, k) \sum_{a} e^{iq \cdot L_a} \psi_n(x, R, k) \\
&= \sum_{a} e^{iq \cdot L_a} \frac{\partial \lambda_n(R, k)}{\partial R_I^{a}} \psi_n(x, R, k) + \lambda_n(R, k) \psi_n^{(1)}(x, R, k, q) \\
&= \lambda_n^{(1)}(R, k, q) \psi_n(x, R, k) + \lambda_n(R, k) \psi_n^{(1)}(x, R, k, q),
\end{aligned}
\]

where we have used the boundary conditions on the Kohn-Sham orbitals (Eq. A44), and the fact that the nonlocal projectors are centered on the atoms, to arrive at Eq. A58.

Therefore, we arrive at the Sternheimer equation:

\[
\left( \mathcal{H}(R, k + q) - \lambda_n(R, k) \mathcal{I} \right) \psi_n^{(1)}(x, R, k, q) = \left( \lambda_n^{(1)}(R, k, q) - \mathcal{H}_n^{(1)}(R, k, q) \right) \psi_n(x, R, k),
\]

where \( \mathcal{H}_n^{(1)} \) is as defined in Eq. 16, and

\[
\lambda_n^{(1)}(R, k, q) = \sum_{a} e^{iq \cdot L_a} \frac{\partial \lambda_n(R, k)}{\partial R_I^{a}} = \frac{\partial \lambda_n(R, k)}{\partial R_I^{0}} \sum_{a} e^{iq \cdot L_a}
= N_0 \delta_{q0} \frac{\partial \lambda_n(R, k)}{\partial R_I^{0}} = \delta_{q0} \lambda_n^{(1)}(R, k, 0),
\]

with \( \lambda_n^{(1)}(R, k, 0) \) derived from Eq. A60 as:

\[
\langle \psi_n(R, k) | \mathcal{H}(R, k) - \lambda_n(R, k) | \psi_n^{(1)}(R, k, 0) \rangle = \langle \psi_n(R, k) | \lambda_n^{(1)}(R, k, q) - \mathcal{H}_n^{(1)}(R, k, q) | \psi_n(R, k) \rangle
\Rightarrow \lambda_n^{(1)}(R, k, 0) = \int_{\Omega} \psi_n^*(x, R, k) \mathcal{H}_n^{(1)}(R, k, 0) \psi_n(x, R, k) \, dx.
\]
the operator $\mathcal{P}_n$ that appears in the non-singular Sternheimer equation (Eq. 24). In the case when $\lambda_n(R, k) \neq \lambda_m(R, k + q)$, the coefficients $\zeta_{n,m}$ can be determined as follows:

$$\left( \mathcal{H}(R, k + q) - \lambda_n(R, k) \right) |\psi_{1,n}(R, k, q)\rangle = \left( \lambda_{n,F_n}(R, k, q) - \mathcal{H}_{1,n}(R, k, q) \right) |\psi_{n}(R, k)\rangle$$

$$\Rightarrow \langle \psi_{m}(R, k + q) | \mathcal{H}(R, k + q) - \lambda_n(R, k) |\psi_{1,n}(R, k, q)\rangle = \langle \psi_{m}(R, k + q) | \mathcal{H}_{1,n}(R, k, q) |\psi_{n}(R, k)\rangle$$

$$\Rightarrow \langle \psi_{m}(R, k + q) | \mathcal{H}_{1,n}(R, k, q) |\psi_{n}(R, k)\rangle = \frac{\gamma_m}{\lambda_n(R, k) - \lambda_m(R, k + q)} \lambda_n(R, k) - \lambda_m(R, k + q)$$

$$\Rightarrow \gamma_m |\psi_{m}(R, k + q)\rangle |\psi_{1,n}(R, k, q)\rangle = \frac{\gamma_m}{\lambda_n(R, k) - \lambda_m(R, k + q)} |\psi_{m}(R, k + q)\rangle |\psi_{n}(R, k)\rangle$$

$$\Rightarrow \zeta_{n,m} = \frac{\gamma_m}{\lambda_n(R, k) - \lambda_m(R, k + q)}, \quad (A63)$$

where the Kohn-Sham eigenvalue equation, the orthogonality between the orbitals for the same wavevector, and $\lambda_{n,F_n}(R, k, 0) = 0$ have been used. The left hand side of the fourth equality corresponds to the action of one of the terms in the operator $\mathcal{Q}$ on $\psi_{1,n}(R, k, q)$. The corresponding coefficient of $\mathcal{P}_n$ is obtained in the fifth equality by comparing the right hand side of fourth equality with the corresponding term in $\mathcal{P}_n \mathcal{H}_{1,n}(R, k) |\psi_n\rangle$, which appears on the right hand side of the nonsingular Sternheimer equation (Eq. 24).

In the case when $\lambda_n(R, k) = \lambda_m(R, k + q)$, the coefficients $\zeta_{n,m}$ cannot be calculated from Eq. A63 since the denominator in the expression vanishes. In this case, following Ref. [35], we first rewrite $\rho_{1,n}$ (Eq. 17) as shown below:

$$\rho_{1,n}(x, R, q) = 2 \int \frac{N_e(k)}{N_e(q)} \left( g_{n,F_n}(R, k, q) |\psi_n(x, R, k)\rangle^2 + g_n(R, k) \psi_n^*(x, R, k) |\psi_{1,n}(x, R, k, q)\rangle \right) dk$$

$$= 2 \int \frac{N_e(k)}{N_e(q)} \left( \sum_{n=1}^{N_e} \left( g_{n,F_n}(R, k, q) |\psi_n(x, R, k)\rangle^2 + \sum_{m=1}^{N_e} g_n(R, k) \psi_n^*(x, R, k) |\psi_{1,n}(x, R, k, q)\rangle \frac{\langle \psi_m(R, k + q) | \mathcal{H}_{1,n}(R, k, q) |\psi_{n}(R, k)\rangle}{\lambda_n(R, k) - \lambda_m(R, k + q)} \right) dk \right.$$
where we have obtained the second equality by expanding \( \psi_{nL_n}^{(1)} \) in terms of the basis of the \( \mathbf{k} \)th space using the coefficients obtained while arriving at Eq. \( \text{A63} \); the third equality is obtained by using the fact that one of the \( \mathbf{k} \) point in the Brillouin zone is the \( \mathbf{k} + \mathbf{q} \) point; the fourth equality is obtained by expanding the series (indexed by \( n \)) to \( N_s \) (since the occupations are zero for the additional states) and interchanging the indices \( n \) and \( m \); the fifth equality is obtained by using the inner product property and adjoint of the \( \mathcal{H}_{L_n} \) operator; the last equality is obtained by using \( g_{n,m} + g_{m,n} = 1 \), \( g_{n,m} = \left( 1 + \exp \left( \frac{\lambda_m - \lambda_n}{k_BT} \right) \right)^{-1} \), and the symmetry of \( n \) and \( m \) indices. Note that the above derivation is not valid in the case of \( \mathbf{q} = 0 \) and \( n = m \), since \( \langle \psi_{nL_n}^{(1)}(\mathbf{k}, 0)|\psi_{nL_n}(\mathbf{k}) \rangle = 0 \) due to normalization constraint on the Kohn-Sham orbitals and hence this state doesn’t appear in the expansion of \( \psi_{nL_n}^{(1)} \).

The expression in Eqn. \( \text{A64} \) confirms the arguments made in previous works \[1, 85\] that \( \rho_{L_n}^{(1)} \) is independent of the coupling between states/orbitals with unit occupations \( g_n = 1 \) or zero occupations \( g_n = 0 \). The second term of Eqq. \( \text{A64} \) can be written as: \( 4 \int_k \sum_{n=1}^{N_s} g_{nL_n}(\mathbf{k}) \psi_{nL_n}(\mathbf{x}, \mathbf{k}) \psi_{nL_n}^{(1)}(\mathbf{x}, \mathbf{k}, \mathbf{q}) \), where \( \psi_{nL_n}^{(1)}(\mathbf{x}, \mathbf{k}, \mathbf{q}) \) satisfies a modified Sternheimer equation \( [3] \), a strategy adopted previously for metallic systems \[3, 35\]. However, in this work we solve the nonsingular Sternheimer equation (Eq. \( \text{A24} \)), and use this expression in Eq. \( \text{A64} \) to instead obtain the coefficients of the projector \( P_n \) in the case when \( \lambda_n(\mathbf{k}) = \lambda_m(\mathbf{k} + \mathbf{q}) \). To do so, we first separate the contribution of degenerate pair of states from the remainder as shown below:

\[
\psi_{nL_n}^{(1)}(\mathbf{x}, \mathbf{k}, \mathbf{q}) = \sum_{m=1}^{N_s} \frac{g_{nL_n}(\mathbf{k}) - g_{mL_n}(\mathbf{k} + \mathbf{q})}{\lambda_n(\mathbf{k}) - \lambda_m(\mathbf{k} + \mathbf{q})} \frac{g_{mL_n}(\mathbf{k} + \mathbf{q})}{g_{nL_n}(\mathbf{k})} \psi_m(\mathbf{x}, \mathbf{k} + \mathbf{q}) \langle \psi_m(\mathbf{k} + \mathbf{q})|\mathcal{H}_{L_n}^{(1)}(\mathbf{k}, \mathbf{q})|\psi_n(\mathbf{k}) \rangle + \frac{1}{2g_{nL_n}(\mathbf{k})} \frac{\partial g_{nL_n}(\mathbf{k})}{\partial \lambda_n(\mathbf{k})} \sum_{m=1}^{N_s} \psi_m(\mathbf{x}, \mathbf{k} + \mathbf{q}) \langle \psi_m(\mathbf{k} + \mathbf{q})|\mathcal{H}_{L_n}^{(1)}(\mathbf{k}, \mathbf{q})|\psi_n(\mathbf{k}) \rangle
\]

(A65)

The second term in the above equation provides the contribution of the degenerate states to the original \( \psi_{nL_n}^{(1)} \), since the components of the two series in the fifth equality of \( \rho_{L_n}^{(1)} \) become identical for degenerate states. Therefore, the coefficients of the projector \( P_n \) corresponding to the degenerate states can be determined by starting from the nonsingular Sternheimer equation and using the same procedure as adopted for the nondegenerate states (Eq. \( \text{A63} \)), thereby giving:

\[
\zeta_{n,m} = 1 - \gamma_m \frac{(1 - g_{nL_n}(\mathbf{k}))}{2k_BT},
\]

(A66)
where we have used the equality
\[
\frac{1}{2g_n(R, k)} \frac{\partial g_n(R, k)}{\partial \lambda_n(R, k)} = -\frac{(1 - g_n(R, k))}{2k_BT}.
\] (A67)

6. Dynamical matrix on \( \hat{\Omega} \)

We now use the above results to reduce the dynamical matrix to the unit cell/fundamental domain \( \hat{\Omega} \). In so doing, we denote the translational symmetry operator as \( \hat{T}_v \), which corresponds to a translation by \( L_a \), i.e., the action (denoted by \( \circ \)) of \( \hat{T}_v \) on any function \( f \) can be written as: \( \hat{T}_v \circ f(x) = f(x - L_a) \).

a. Variational contribution The variational contribution to the dynamical matrix (Eq. A30) is reduced to \( \hat{\Omega} \) as follows:

\[
\hat{\mathcal{C}}_{nn}^{\text{var}}(R, q) = \frac{1}{N^2} \sum_{k=1}^{N_v} \sum_{n=1}^{N_v} g_n(R, k) \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right)
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, -q) \left( H(R, k - q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, -q) dx \right)
\]

\[
= \frac{1}{N^2} \sum_{n=1}^{N_v} g_n(R, k) \left( \sum_{n=1}^{N_v} \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right) 
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, -q) \left( H(R, k - q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, -q) dx \right) \right) dk
\]

\[
= 2 \sum_{n=1}^{N_v} g_n(R, k) \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right)
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, -q) \left( H(R, k - q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, -q) dx \right) \right) dk
\]

\[
= 2 \sum_{n=1}^{N_v} g_n(R, k) \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, -k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right)
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, -k, q) \left( H(R, -k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, -k, q) dx \right) \right) dk
\]

\[
= 2 \sum_{n=1}^{N_v} g_n(R, k) \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, -k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right)
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, -k, q) \left( H(R, -k + q) - \lambda_n(R, k) \right) \psi_{n,\beta}^{(1)}(x, R, -k, q) dx \right) \right) dk
\]

\[
= -2 \sum_{n=1}^{N_v} g_n(R, k) \left( \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, k, q) \left( H(R, k, q) \right) \psi_{n,\beta}^{(1)}(x, R, k, q) dx \right) \right)
\]

\[
+ \int_{\hat{\Omega}} \left( \psi_{n,\alpha}^{(1)}(x, R, -k, q) \left( H(R, -k, q) \right) \psi_{n,\beta}^{(1)}(x, R, -k, q) dx \right) \right) \right) dk,
\] (A68)

where the third equality is obtained by using the commutation of the Hamiltonian with translation operators, and the boundary conditions satisfied by \( \psi_{n,\alpha}^{(1)} \) (Eq. A43); the fourth equality is obtained by using the inner product property and the Hermitian nature of the Hamiltonian; the fifth equality is obtained by using the time-reversal symmetry in the absence of external magnetic field, whereby \( \psi_{n,\alpha}^{(1)} \) satisfy the following relationship:

\[
\psi_{n,\alpha}^{(1)*}(x, R, k, q) = \psi_{n,\alpha}^{(1)*}(x, R, -k, q);
\] (A69)

and the last equality is obtained by using the nonsingular Sternheimer equation (Eq. 24) and the orthonormality of \( \psi_{n,\alpha}^{(1)} \) with \( \psi_n \) for \( q = 0 \). This reformulation has computational advantages as it makes the computation of a
dynamical matrix entry to depend only on the $\psi_{n_{R}}^{(1)}$ corresponding to that perturbation and hence does not require the storage of all $\psi_{n_{R}}^{(1)}$, which provides significant reduction in computer memory requirements.

b. Exchange-correlation contribution  The exchange-correlation contribution to the dynamical matrix (Eq. A31) is reduced to $\hat{\Omega}$ as follows:

$$
\hat{c}_{\hat{I}_{R}, \hat{J}_{R}}^{xc}(\mathbf{R}, \mathbf{q}) = \frac{1}{N_c} \sum_{\mathbf{T}_{\Omega}} \int_{\mathbf{T}_{\Omega} \in \Omega} \rho_{\hat{I}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \left( 2 \frac{\partial \varepsilon_{xc}(\rho(\mathbf{q}, \mathbf{R}))}{\partial \rho(\mathbf{R})} + \rho(\mathbf{R}) \frac{\partial^{2} \varepsilon_{xc}(\rho(\mathbf{q}, \mathbf{R}))}{\partial \rho(\mathbf{R})^{2}} \right) \rho_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x}
$$

$$
= \int_{\Omega} \rho_{\hat{I}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \left( 2 \frac{\partial \varepsilon_{xc}(\rho(\mathbf{q}, \mathbf{R}))}{\partial \rho(\mathbf{R})} + \rho(\mathbf{R}) \frac{\partial^{2} \varepsilon_{xc}(\rho(\mathbf{q}, \mathbf{R}))}{\partial \rho(\mathbf{R})^{2}} \right) \rho_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x},
$$

(A70)

where we have used the periodicity of the electron density (Eq. A37), and the Bloch-periodicity of $\rho_{\hat{I}_{R}}^{(1)}$ (Eq. A36).

c. Electrostatics contribution  The electrostatic contribution to the dynamical matrix (Eq. A32) is reduced to $\hat{\Omega}$ as follows:

$$
\hat{c}_{\hat{I}_{R}, \hat{J}_{R}}^{\text{elec}}(\mathbf{R}, \mathbf{q}) = \frac{1}{2 N_c} \sum_{\mathbf{T}_{\Omega}} \left( 2 \delta_{IJ} \int_{\mathbf{T}_{\Omega} \in \Omega} \nabla_{\alpha} \nabla_{\beta} b_{J}(\mathbf{x}, \mathbf{R}^{b}_{\mathbf{R}}) \phi(\mathbf{R}, \mathbf{q}) \, d\mathbf{x} + \int_{\mathbf{T}_{\Omega} \in \Omega} \left( \rho_{\hat{I}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) + \rho_{\hat{J}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \right) \right)
$$

$$
\times \phi_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x} + \int_{\mathbf{T}_{\Omega} \in \Omega} \phi_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \left( \rho_{\hat{I}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) + b_{\hat{J}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \right) \, d\mathbf{x} + \int_{\mathbf{T}_{\Omega} \in \Omega} \sum_{\alpha} e^{-iq_{L_{\alpha}}(\nabla_{\alpha} b_{J}(\mathbf{x}, \mathbf{R}^{b}_{\mathbf{R}}))}
$$

$$
\times \phi_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x} + \int_{\mathbf{T}_{\Omega} \in \Omega} \rho_{\hat{I}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \left( 2 \frac{\partial \varepsilon_{xc}(\rho(\mathbf{R}, \mathbf{q}))}{\partial \rho(\mathbf{R})} + \rho(\mathbf{R}) \frac{\partial^{2} \varepsilon_{xc}(\rho(\mathbf{R}, \mathbf{q}))}{\partial \rho(\mathbf{R})^{2}} \right) \rho_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x},
$$

(A70)

$$
\times \phi_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x} + \int_{\mathbf{T}_{\Omega} \in \Omega} \rho_{\hat{I}_{R}}^{(1)*}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \left( 2 \frac{\partial \varepsilon_{xc}(\rho(\mathbf{R}, \mathbf{q}))}{\partial \rho(\mathbf{R})} + \rho(\mathbf{R}) \frac{\partial^{2} \varepsilon_{xc}(\rho(\mathbf{R}, \mathbf{q}))}{\partial \rho(\mathbf{R})^{2}} \right) \rho_{\hat{J}_{R}}^{(1)}(\mathbf{x}, \mathbf{R}, \mathbf{q}) \, d\mathbf{x}.
$$

(A70)
where the second equality is obtained by using the periodic nature of the electrostatic potential (Eq. A42), periodicity associated with the pseudocharge potential and density due to an atom and all its images, Bloch-periodic nature of divergence theorem and integration by parts.

The nonlocal pseudopotential contribution to the dynamical matrix $A_{33}$ on $\hat{\Omega}$ is derived to be:

$$\hat{C}^{nl}_{I_a, J_b} (\mathbf{R}, \mathbf{q}) = -2 \sum_{\mathbf{k}} \sum_{n=1}^{N_{\mathbf{k}}(k)} \left( 2g_{n_{I_a}(k)}^{(1)} (\mathbf{R}, \mathbf{k}, \mathbf{q}) \sum_{p=1}^{p_I} \gamma_{I_J(p)} \left( \sum_e \left( \int_{\hat{\Omega}} \psi_n^* (\mathbf{x}, \mathbf{R}, \mathbf{k}) e^{i k_L e} \nabla_\beta \chi_{J(p)} (\mathbf{x}, \mathbf{R}_J^d) \, d\mathbf{x} \right) \right) \right) \times \delta_{IJ}(1) \int_{\hat{\Omega}} \left( \nabla_\alpha \hat{V} (\mathbf{x}, \mathbf{R}_J^d) - \nabla_\alpha V (\mathbf{x}, \mathbf{R}_J^b) \right) \, d\mathbf{x} - \frac{\delta_{IJ}}{2} \sum_{b} \int_{\hat{\Omega}} \nabla_\alpha \left( \hat{b}(\mathbf{x}, \mathbf{R}) + \hat{b}(\mathbf{x}, \mathbf{R}) \right) \left( \nabla_\beta \hat{V} (\mathbf{x}, \mathbf{R}_J^b) - \nabla_\beta V (\mathbf{x}, \mathbf{R}_J^b) \right) \, d\mathbf{x} \right),$$

where $\hat{C}^{nl}_{I_a, J_b} (\mathbf{R}, \mathbf{q})$ is the nonlocal pseudopotential contribution to the dynamical matrix on $\hat{\Omega}$.

d. Nonlocal pseudopotential contribution The nonlocal pseudopotential contribution to the dynamical matrix (Eq. A33) on $\hat{\Omega}$ is derived to be:

$$\hat{C}^{nl}_{I_a, J_b} (\mathbf{R}, \mathbf{q}) = -2 \sum_{\mathbf{k}} \sum_{n=1}^{N_{\mathbf{k}}(k)} \left( 2g_{n_{I_a}(k)}^{(1)} (\mathbf{R}, \mathbf{k}, \mathbf{q}) \sum_{p=1}^{p_I} \gamma_{I_J(p)} \left( \sum_e \left( \int_{\hat{\Omega}} \psi_n^* (\mathbf{x}, \mathbf{R}, \mathbf{k}) e^{i k_L e} \nabla_\beta \chi_{J(p)} (\mathbf{x}, \mathbf{R}_J^d) \, d\mathbf{x} \right) \right) \right) \times \delta_{IJ}(1) \int_{\hat{\Omega}} \left( \nabla_\alpha \hat{V} (\mathbf{x}, \mathbf{R}_J^d) - \nabla_\alpha V (\mathbf{x}, \mathbf{R}_J^b) \right) \, d\mathbf{x} - \frac{\delta_{IJ}}{2} \sum_{b} \int_{\hat{\Omega}} \nabla_\alpha \left( \hat{b}(\mathbf{x}, \mathbf{R}) + \hat{b}(\mathbf{x}, \mathbf{R}) \right) \left( \nabla_\beta \hat{V} (\mathbf{x}, \mathbf{R}_J^b) - \nabla_\beta V (\mathbf{x}, \mathbf{R}_J^b) \right) \, d\mathbf{x} \right),$$

where $\hat{C}^{nl}_{I_a, J_b} (\mathbf{R}, \mathbf{q})$ is the nonlocal pseudopotential contribution to the dynamical matrix on $\hat{\Omega}$.
with the projector's dependence on the atomic position.

\[
\psi_n(x, R, k) e^{-i k L_a} \, dx \right) + \sum_{p=1}^{p_d} \sum_{\alpha=I_{J,p}} \sum_{a} \sum_{\beta=I_{J,p}} \sum_{c} \left( \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R, k, q) e^{-i(k+q) L_e} \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{d}) \, dx \right)
\]

\[
\times \psi_n(x, R, k) \int_{\Omega} \sum_{a} \sum_{\beta=I_{J,p}} \sum_{c} \left( \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R, k, q) e^{-i(-k+q) L_a} \, dx \right) \, dk,
\]

where each term in the above equation is the reduction of the equivalent term in Eq. A33, with the \( D_{10} \) term reduced to \( \Omega \) using the following procedure (representative of the reduction for the other terms, i.e., \( D_6, D_7, D_8, D_9, D_{11}, D_{12}, \) and \( D_{13} \)):

\[
D_{10}(R) = -\frac{1}{N_e} \sum_{k=1}^{N_c} \sum_{n=1}^{N_t} g_n(R, k) \sum_{p=1}^{p_d} \sum_{\alpha=I_{J,p}} \sum_{a} \sum_{\beta=I_{J,p}} \sum_{c} \left( \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R, k) \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \, dx \right) \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R_{j}^{a}) \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \, dx \right)
\]

\[
\times \psi_{n,I_{J,p}}^{*}(x, R, k, q) e^{-i(q) L_c} \sum_{a} \sum_{\beta=I_{J,p}} \sum_{c} \left( \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R, k) e^{-i(k+q) L_e} \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \, dx \right) \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \psi_{n}(x, R, k) \, dx \right) \, dk
\]

\[
= -\frac{1}{N_e} \sum_{k=1}^{N_c} \sum_{n=1}^{N_t} g_n(R, k) \sum_{p=1}^{p_d} \sum_{\alpha=I_{J,p}} \sum_{a} \sum_{\beta=I_{J,p}} \sum_{c} \left( \int_{\Omega} \psi_{n,I_{J,p}}^{*}(x, R, k) e^{-i(k+q) L_a} \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \, dx \right) \nabla_{\alpha} \chi_{J:p}(x, R_{j}^{a}) \psi_{n}(x, R, k) \, dx \right) \, dk
\]

\[
= \left( \sum_{d} \int_{\Omega} \chi_{I_{J,p}}^{*} \psi_{n,I_{J,p}}^{*}(x, R_{j}^{a-d}) \psi_{n,I_{J,p}}^{*}(x, R_{j}^{a-d}) \, dx \right) \psi_{n,I_{J,p}}^{*}(x, R, k, q) e^{i(k+q) L_d} \, dx \right) \, dk
\]

with the fourth equality obtained by multiplying the phase factor and its conjugate to make the summations consistent with the projector’s dependence on the atomic position.
We now show that the developed real-space DFPT formulation and implementation can also be used for calculating the vibrational spectra of isolated systems, taking the silane molecule (SiH$_4$) as a representative example. In particular, we compute the vibrational frequencies of silane at the equilibrium Si–H bond length of 2.04 Bohr, using both ABINIT and the M-SPARC implementation developed for the proposed real-space formulation. For this purpose, we use a mesh size of 0.2 Bohr in M-SPARC and a planewave cutoff of 40 Ha in ABINIT. The results so obtained are presented in Table I. It is clear that there is very good agreement between M-SPARC and ABINIT, with the maximum difference in the frequencies being 0.52 cm$^{-1}$. In addition, there is very good agreement in the zero-point energy — half of the sum of all the phonon frequencies — with the difference being M-SPARC and ABINIT being 1.57 cm$^{-1}$. These results verify the accuracy of the proposed DFPT formulation/implementation for isolated clusters/molecules.

### Appendix B: Vibrational spectrum for the silane molecule

|                  | symmetric stretch (1) | symmetric bend (2) | asymmetric stretch (3) | asymmetric bend (3) |
|------------------|-----------------------|--------------------|------------------------|---------------------|
| M-SPARC          | 2155.01               | 932.93             | 2176.11                | 850.58              |
| ABINIT           | 2155.52               | 933.23             | 2176.27                | 851.10              |

TABLE I: Vibrational frequencies (in cm$^{-1}$) for the silane molecule, as computed by M-SPARC and ABINIT. The number in brackets represents the degeneracy associated with that mode.

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