Direct calculation of static response functions using non-diagonal supercell matrices

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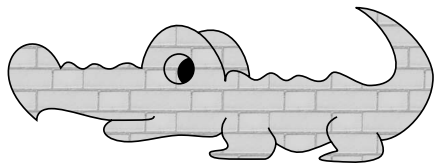

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Introduction

- Many properties of materials are determined by the variation of the total energy around the equilibrium configuration of the system.
- Vast amounts of experimental data have been generated from studies of vibrational spectra, magnetic excitations, and other responses to experimental probes.
- First principles calculations have been successfully used to provide improved understanding of experimental discoveries and to predict novel properties and behaviour before they have been observed.

Static response functions

$$\frac{\partial \,\text{observable}}{\partial \,\text{perturbation}}$$

$$\text{Force constants} \approx \frac{\partial F_{\alpha i}}{\partial u_{\beta j}} \qquad \text{Born effective charges} \approx \frac{\partial P_i}{\partial u_{\beta j}}$$

$$\text{Elastic constants} \approx \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \qquad \text{Piezoelectric constants} \approx \frac{\partial P_i}{\partial \epsilon_{kl}}$$

- The response of periodic systems to perturbations characterised by a wave vector $\mathbf{k}$ may be calculated using the direct method or perturbative methods.

The direct method

- The direct method involve freezing a perturbation into a system and calculating the response functions using a finite difference approach.
- The formalism is conceptually straightforward but only perturbations commensurate with the simulation cell can be considered.
- This necessitates the use of supercells and the computational cost increases rapidly with system size.
- The simplicity of the direct method means that it is often utilised in the early development of a new field of research.

Perturbative methods

- Perturbative methods involve determining the linear response of a system with respect to a perturbation of a given wave vector.
- It is possible to consider perturbations that are not commensurate with the periodic lattice using a single primitive cell.
- Perturbative methods have therefore been used for the majority of calculations of response functions for solids.
- It requires significant effort to implement linear response methods for a new physical quantity of interest.

Supercells

- A supercell is the unit cell of a superlattice, whose basis vectors are constructed by taking linear combinations of the primitive lattice basis vectors with integer coefficients.

$$\begin{pmatrix} \mathbf{a}_{\mathrm{s}_1} \\ \mathbf{a}_{\mathrm{s}_2} \\ \mathbf{a}_{\mathrm{s}_3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}_{\mathrm{p}_1} \\ \mathbf{a}_{\mathrm{p}_2} \\ \mathbf{a}_{\mathrm{p}_3} \end{pmatrix}$$

$$S_{ij} \in \mathbb{Z}$$

- The supercell contains $|S|$ parent primitive cells. We refer to the matrix S as the supercell matrix.

Reciprocal space

- The set of plane waves with the same periodicity as the primitive lattice define the reciprocal primitive lattice.

$$\begin{pmatrix} \mathbf{b}_{\mathsf{p}_1} \\ \mathbf{b}_{\mathsf{p}_2} \\ \mathbf{b}_{\mathsf{p}_3} \end{pmatrix} = 2\pi \begin{pmatrix} \mathbf{a}_{\mathsf{p}_1} \\ \mathbf{a}_{\mathsf{p}_2} \\ \mathbf{a}_{\mathsf{p}_3} \end{pmatrix}^{-\mathsf{T}}$$

- The set of plane waves with the same periodicity as the superlattice define the reciprocal superlattice.

$$\begin{pmatrix} \mathbf{b}_{\mathsf{s}_1} \\ \mathbf{b}_{\mathsf{s}_2} \\ \mathbf{b}_{\mathsf{s}_3} \end{pmatrix} = \begin{pmatrix} \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{13} \\ \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{23} \\ \bar{S}_{31} & \bar{S}_{32} & \bar{S}_{33} \end{pmatrix} \begin{pmatrix} \mathbf{b}_{\mathsf{p}_1} \\ \mathbf{b}_{\mathsf{p}_2} \\ \mathbf{b}_{\mathsf{p}_3} \end{pmatrix}$$

$$\bar{S}_{ij} = (S^{-1})_{ji}$$

Fractional coordinates

- An arbitrary $\mathbf{k}$-point can be expressed in terms of both the reciprocal primitive lattice basis vectors and reciprocal superlattice basis vectors.

$$\begin{pmatrix} k_{\mathsf{s}_1} \\ k_{\mathsf{s}_2} \\ k_{\mathsf{s}_3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} k_{\mathsf{p}_1} \\ k_{\mathsf{p}_2} \\ k_{\mathsf{p}_3} \end{pmatrix}$$

- If the reciprocal superlattice fractional coordinates are all integers, collective displacements of atoms characterised by the wave vector $\mathbf{k}$ are commensurate with the supercell defined by S.

A change of basis

$$
\begin{aligned}
\mathbf{R}_{n_1 n_2 n_3} &= n_1 \mathbf{a}_{s_1} + n_2 \mathbf{a}_{s_2} + n_3 \mathbf{a}_{s_3} \\
&= (n_1 - n_3)\mathbf{a}_{s_1} + n_2 \mathbf{a}_{s_2} + n_3(\mathbf{a}_{s_1} + \mathbf{a}_{s_3}) \\
&= n'_1 \mathbf{a}'_{s_1} + n'_2 \mathbf{a}'_{s_2} + n'_3 \mathbf{a}'_{s_3} \\
&= \mathbf{R}_{n'_1 n'_2 n'_3}
\end{aligned}
$$

- There are a finite number of unique superlattices with unit cells that contain a given number of primitive cells, but there are an infinite number of sets of basis vectors that can be used to describe each superlattice.
- Two different supercell matrices S and S' generate different bases for the same superlattice if S' can be reduced to S by elementary unimodular row operations.

Hermite normal form

- The canonical form for elementary unimodular row operations is the upper-triangular Hermite normal form (HNF):

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} \\ 0 & S_{22} & S_{23} \\ 0 & 0 & S_{33} \end{pmatrix}$$

$$0 \leq S_{12} < S_{22} \text{ and } 0 \leq S_{13}, S_{23} < S_{33}$$

- Note that the product $S_{11}S_{22}S_{33}$ fixes the determinant $|S|$ and therefore the number of primitive unit cells contained within the supercell.
- Most previous calculations have used supercell matrices with $S_{12} = S_{13} = S_{23} = 0$.

Commensurate k-points

$$\begin{pmatrix} k_{\mathsf{p}_1} \\ k_{\mathsf{p}_2} \\ k_{\mathsf{p}_3} \end{pmatrix} = \begin{pmatrix} \frac{m_1}{n_1} \\ \frac{m_2}{n_2} \\ \frac{m_3}{n_3} \end{pmatrix}$$

$$0 \leq k_{\mathsf{p}_1}, k_{\mathsf{p}_2}, k_{\mathsf{p}_3} < 1$$

$m_1/n_1,\ m_2/n_2,$ and m_3/n_3 are reduced fractions

$$\begin{aligned} k_{\mathsf{s}_1} &= \frac{S_{11}m_1}{n_1} + \frac{S_{12}m_2}{n_2} + \frac{S_{13}m_3}{n_3} \\ k_{\mathsf{s}_2} &= \frac{S_{22}m_2}{n_2} + \frac{S_{23}m_3}{n_3} \\ k_{\mathsf{s}_3} &= \frac{S_{33}m_3}{n_3} \end{aligned}$$

Diagonal supercell matrices

$$k_{\mathsf{s}_1} = \frac{S_{11} m_1}{n_1}$$
$$k_{\mathsf{s}_2} = \frac{S_{22} m_2}{n_2}$$
$$k_{\mathsf{s}_3} = \frac{S_{33} m_3}{n_3}$$

$$|S| = n_1 n_2 n_3$$

- $\mathbf{k}$-points on an $N \times N \times N$ grid. Size of largest supercell required scales as N^3. Cost of standard DFT calculation scales as N^9.

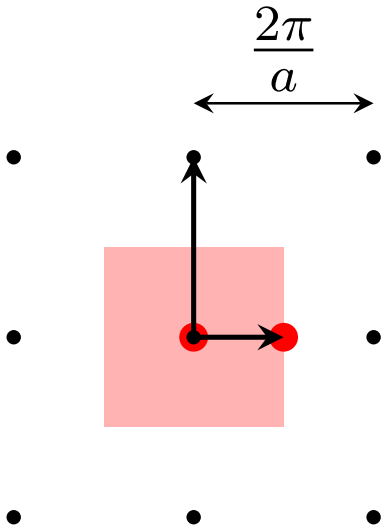
Non-diagonal supercell matrices

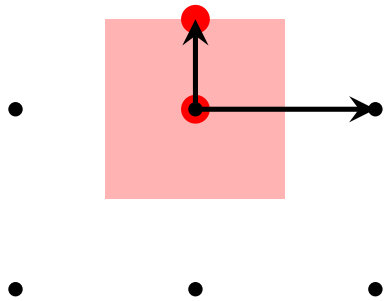
$$k_{\mathsf{s}_1} = \frac{S_{11}m_1}{n_1} + \frac{S_{12}m_2}{n_2} + \frac{S_{13}m_3}{n_3}$$
$$k_{\mathsf{s}_2} = \frac{S_{22}m_2}{n_2} + \frac{S_{23}m_3}{n_3}$$
$$k_{\mathsf{s}_3} = \frac{S_{33}m_3}{n_3}$$

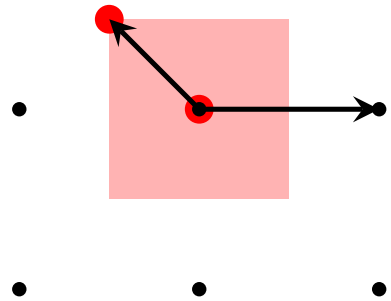
$$|S| = \mathsf{lcm}(n_1, n_2, n_3)$$

- $\mathbf{k}$-points on an $N \times N \times N$ grid. Size of largest supercell required scales as N. Cost of standard DFT calculation scales as N^3.

Two-dimensional example







$$S = \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix} \qquad S = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix} \qquad S = \begin{pmatrix} 1 & 1 \\ 0 & 2 \end{pmatrix}$$

$$\bar{S} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & 1 \end{pmatrix} \qquad \bar{S} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \qquad \bar{S} = \begin{pmatrix} 1 & 0 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

Lattice dynamics

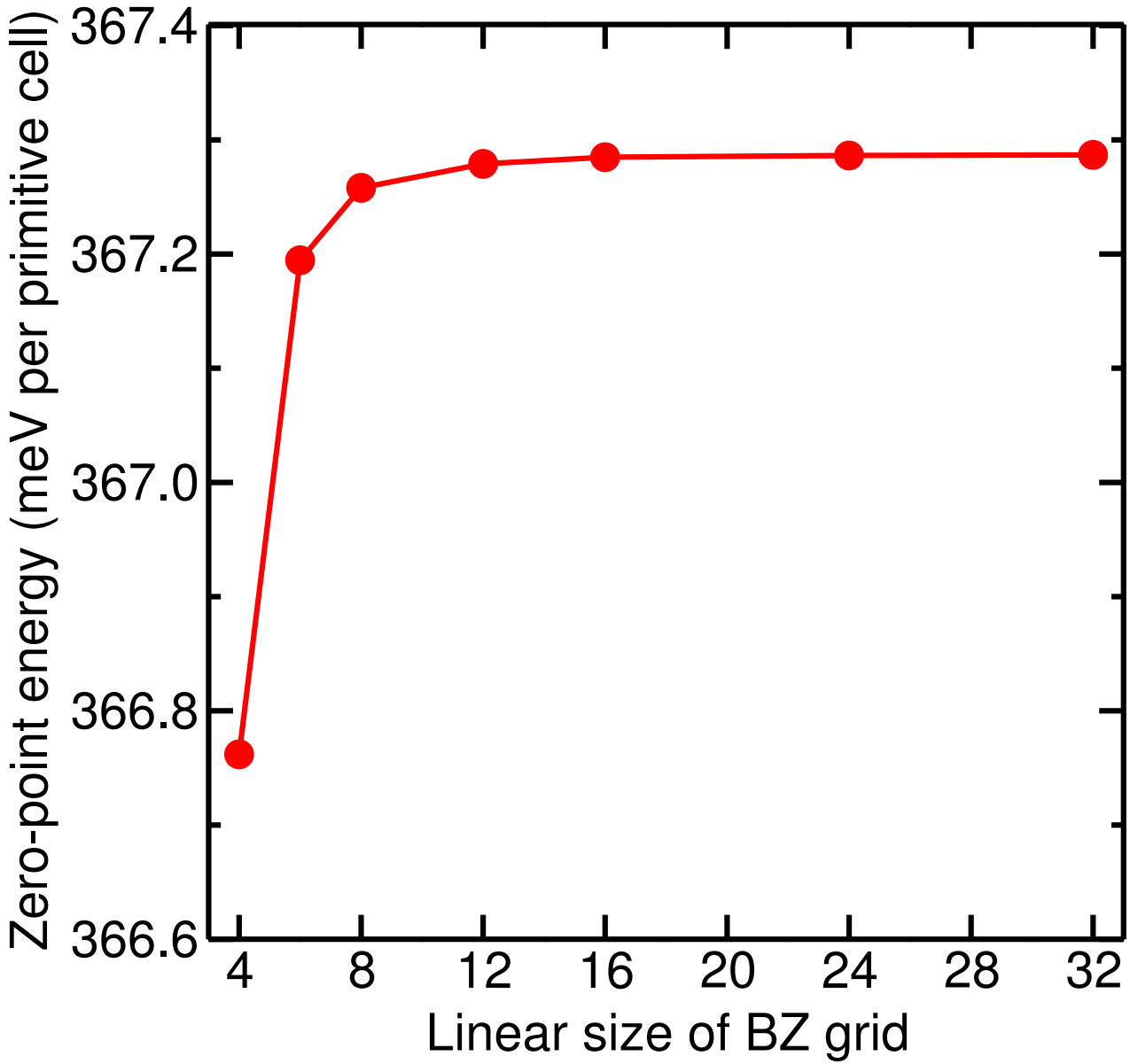
$$E(\mathbf{r}) = E(\mathbf{r}^0) + \frac{1}{2} \sum_{\substack{\mathbf{R}_p,\alpha,i \\ \mathbf{R}_{p'},\alpha',i'}} C_{\alpha i \alpha' i'}(\mathbf{R}_p - \mathbf{R}_{p'}) u_{p\alpha i} u_{p'\alpha' i'}$$

$$C_{\alpha i \alpha' i'}(\mathbf{R}_p - \mathbf{R}_{p'}) = \frac{\partial^2 E(\mathbf{r^0})}{\partial u_{p\alpha i} \partial u_{p'\alpha' i'}}$$

$$D_{\alpha i \alpha' i'}(\mathbf{k}) = \frac{1}{\sqrt{m_\alpha m_{\alpha'}}} \sum_{\mathbf{R}_p} C_{\alpha i \alpha' i'}(\mathbf{R}_p) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_p}$$

$$\hat{H}_{\mathsf{vib}} = -\frac{1}{2} \sum_{n,\mathbf{k}} \frac{\partial^2}{\partial q_{n\mathbf{k}}^2} + \frac{1}{2} \sum_{n,\mathbf{k}} \omega_{n\mathbf{k}}^2 q_{n\mathbf{k}}^2$$

Zero-point vibrational energy of diamond



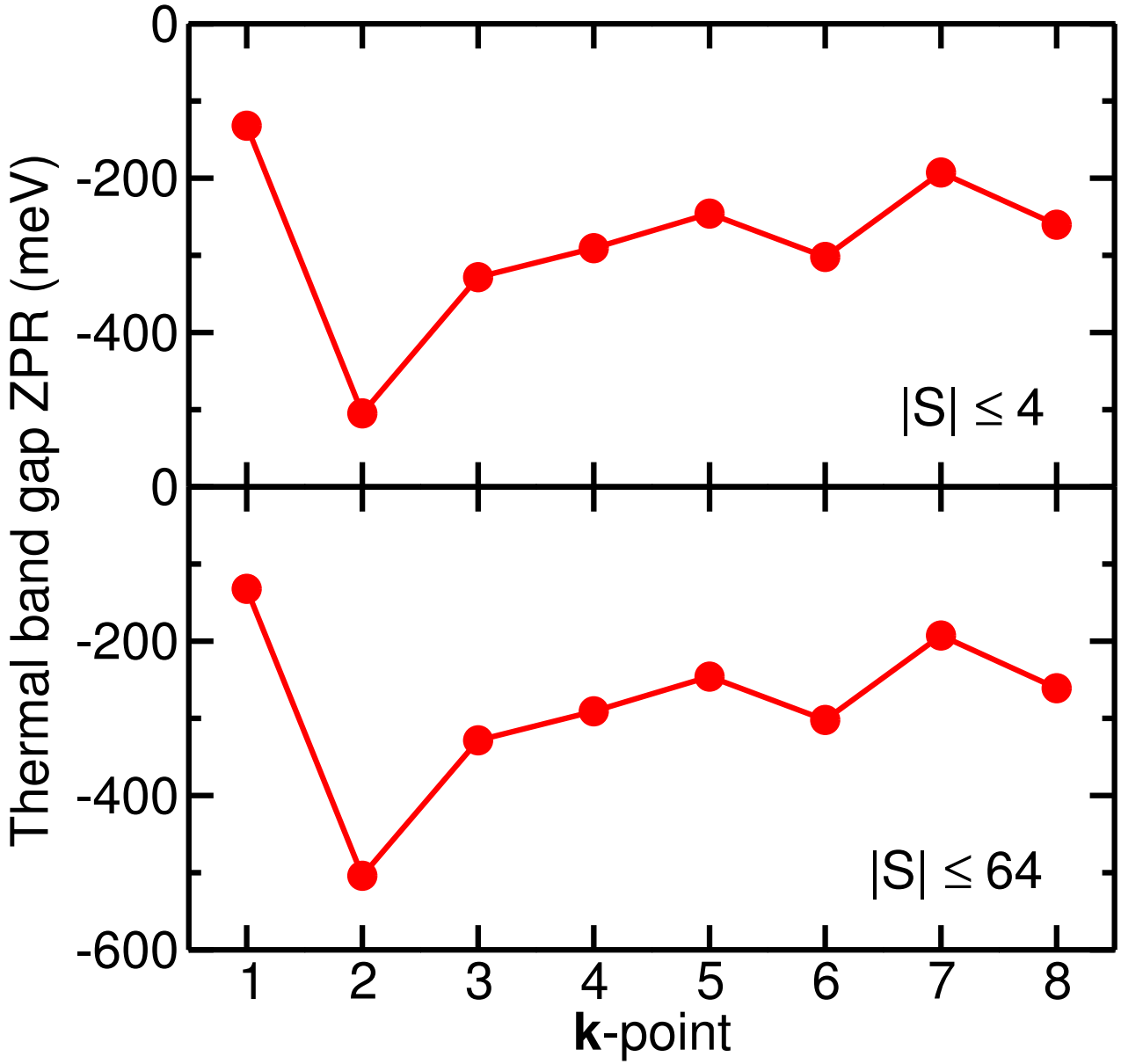
Electron-phonon coupling

$$\langle E_{\mathrm{g}} \rangle = \langle \Phi(\mathbf{q}) | E_{\mathrm{g}}(\mathbf{q}) | \Phi(\mathbf{q}) \rangle$$

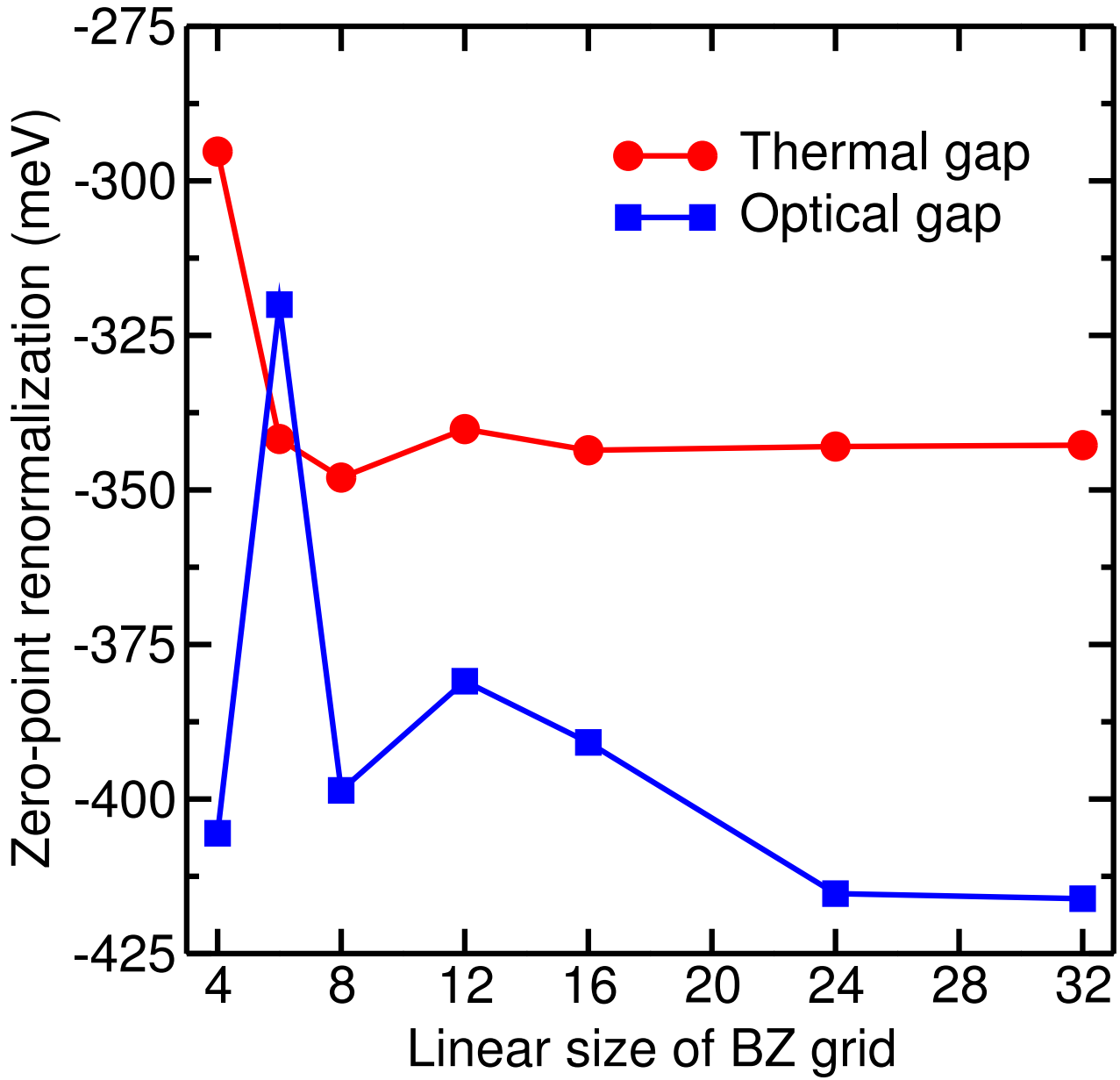
$$E_{\mathrm{g}}(\mathbf{q}) = E_{\mathrm{g}}(\mathbf{0}) + \sum_{n,\mathbf{k}} c^{(1)}_{n\mathbf{k}} q_{n\mathbf{k}} + \sum_{\substack{n,\mathbf{k} \\ n',\mathbf{k}'}} c^{(2)}_{n\mathbf{k};n'\mathbf{k}'} q_{n\mathbf{k}} q_{n'\mathbf{k}'} + \cdots$$

$$E_{\mathrm{ZPR}} = \sum_{n,\mathbf{k}} \frac{c^{(2)}_{n\mathbf{k};n\mathbf{k}}}{2\omega_{n\mathbf{k}}}$$

Comparison using $4 \times 4 \times 4$ grids



Thermal and optical band gaps of diamond



Some numbers

- We have considered $\mathbf{k}$-point grids up to $32 \times 32 \times 32$. The largest supercells that we have used contained 32 primitive cells.
- If we had only considered diagonal supercell matrices, we would have needed to use supercells containing $32^3 = 32,768$ primitive cells.

Conclusions

- The responses of condensed matter systems to perturbations characterized by a wave vector $\mathbf{k}$ are central in probing a wide range of physical properties.
- The use of non-diagonal supercell matrices significantly reduces the computational cost of calculating response functions using the direct method.
- The direct method may now be applied to problems that were previously only tractable using perturbative methods.
- Paper coming soon!