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

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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

\[
\frac{\partial \text{observable}}{\partial \text{perturbation}}
\]

Force constants \( \approx \frac{\partial F_{\alpha i}}{\partial u_{\beta j}} \)

Born effective charges \( \approx \frac{\partial P_i}{\partial u_{\beta j}} \)

Elastic constants \( \approx \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \)

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.

\[
\begin{pmatrix}
a_{s1} \\
a_{s2} \\
a_{s3}
\end{pmatrix} =
\begin{pmatrix}
S_{11} & S_{12} & S_{13} \\
S_{21} & S_{22} & S_{23} \\
S_{31} & S_{32} & S_{33}
\end{pmatrix}
\begin{pmatrix}
a_{p1} \\
a_{p2} \\
a_{p3}
\end{pmatrix}
\]

\[S_{ij} \in \mathbb{Z}\]

- 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.

\[
\begin{pmatrix}
    b_{p1} \\
    b_{p2} \\
    b_{p3}
\end{pmatrix} = 2\pi \begin{pmatrix}
    a_{p1} \\
    a_{p2} \\
    a_{p3}
\end{pmatrix}^{-T}
\]

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

\[
\begin{pmatrix}
    b_{s1} \\
    b_{s2} \\
    b_{s3}
\end{pmatrix} = \begin{pmatrix}
    \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{13} \\
    \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{23} \\
    \bar{S}_{31} & \bar{S}_{32} & \bar{S}_{33}
\end{pmatrix}\begin{pmatrix}
    b_{p1} \\
    b_{p2} \\
    b_{p3}
\end{pmatrix}
\]

\[
\bar{S}_{ij} = (S^{-1})_{ji}
\]
Fractional coordinates

- An arbitrary \( k \)-point can be expressed in terms of both the reciprocal primitive lattice basis vectors and reciprocal superlattice basis vectors.

\[
\begin{pmatrix}
k_{s1} \\
k_{s2} \\
k_{s3}
\end{pmatrix}
=
\begin{pmatrix}
S_{11} & S_{12} & S_{13} \\
S_{21} & S_{22} & S_{23} \\
S_{31} & S_{32} & S_{33}
\end{pmatrix}
\begin{pmatrix}
k_{p1} \\
k_{p2} \\
k_{p3}
\end{pmatrix}
\]

- If the reciprocal superlattice fractional coordinates are all integers, collective displacements of atoms characterised by the wave vector \( k \) are commensurate with the supercell defined by \( S \).
A change of basis

\[ \mathbf{R}_{n_1n_2n_3} = n_1 \mathbf{a}_s_1 + n_2 \mathbf{a}_s_2 + n_3 \mathbf{a}_s_3 \]
\[ = (n_1 - n_3) \mathbf{a}_s_1 + n_2 \mathbf{a}_s_2 + n_3 (\mathbf{a}_s_1 + \mathbf{a}_s_3) \]
\[ = n'_1 \mathbf{a'}_s_1 + n'_2 \mathbf{a'}_s_2 + n'_3 \mathbf{a'}_s_3 \]
\[ = \mathbf{R}_{n'_1n'_2n'_3} \]

- 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.

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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

\[
\begin{pmatrix}
k_{p_1} \\
k_{p_2} \\
k_{p_3}
\end{pmatrix} = 
\begin{pmatrix}
m_1 \\
n_1 \\
m_2 \\
n_2 \\
m_3 \\
n_3
\end{pmatrix}
\]

\[0 \leq k_{p_1}, k_{p_2}, k_{p_3} < 1\]

\(m_1/n_1, m_2/n_2, \text{ and } m_3/n_3\) are reduced fractions

\[
k_{s_1} = \frac{S_{11}m_1}{n_1} + \frac{S_{12}m_2}{n_2} + \frac{S_{13}m_3}{n_3}
\]

\[
k_{s_2} = \frac{S_{22}m_2}{n_2} + \frac{S_{23}m_3}{n_3}
\]

\[
k_{s_3} = \frac{S_{33}m_3}{n_3}
\]
Diagonal supercell matrices

\[ k_{s_1} = \frac{S_{11}m_1}{n_1} \]
\[ k_{s_2} = \frac{S_{22}m_2}{n_2} \]
\[ k_{s_3} = \frac{S_{33}m_3}{n_3} \]

\[ |S| = n_1n_2n_3 \]

- 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

\[ k_{s_1} = \frac{S_{11} m_1}{n_1} + \frac{S_{12} m_2}{n_2} + \frac{S_{13} m_3}{n_3} \]

\[ k_{s_2} = \frac{S_{22} m_2}{n_2} + \frac{S_{23} m_3}{n_3} \]

\[ k_{s_3} = \frac{S_{33} m_3}{n_3} \]

\[ |S| = \text{lcm}(n_1, n_2, n_3) \]

- \( k \)-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

\[
\bar{S} = \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}
\]

\[
S = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}
\]

\[
\bar{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

\[
S = \begin{pmatrix} 1 & 1 \\ 0 & 2 \end{pmatrix}
\]
Lattice dynamics

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

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

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

\[ \hat{H}_{\text{vib}} = -\frac{1}{2} \sum_{n, \mathbf{k}} \frac{\partial^2}{\partial q_{n \mathbf{k}}^2} + \frac{1}{2} \sum_{n, \mathbf{k}} \omega_{n \mathbf{k}}^2 q_{n \mathbf{k}}^2 \]
Zero-point vibrational energy of diamond

![Graph showing the relationship between linear size of BZ grid and zero-point energy (meV per primitive cell). The graph indicates a sharp increase in energy until a linear size of approximately 8, after which the energy stabilizes.

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Electron-phonon coupling

\[ \langle E_g \rangle = \langle \Phi(q)|E_g(q)|\Phi(q) \rangle \]

\[ E_g(q) = E_g(0) + \sum_{n,k} c^{(1)}_{nk} q_{nk} + \sum_{n,k} c^{(2)}_{nk;n'k'} q_{nk} q_{n'k'} + \cdots \]

\[ E_{ZPR} = \sum_{n,k} \frac{c^{(2)}_{nk;nk}}{2\omega_{nk}} \]
Comparison using $4 \times 4 \times 4$ grids

Thermal band gap ZPR (meV) vs. k-point for different values of $|S|$: $|S| \leq 4$ and $|S| \leq 64$. The graph shows a trend where the thermal band gap decreases significantly at certain k-point values, especially noticeable for $|S| \leq 4$. The ESDG – June 2015 note indicates the source of the data.
Thermal and optical band gaps of diamond.
Some numbers

- We have considered $k$-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 $k$ 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!