The search for the optimal supercell

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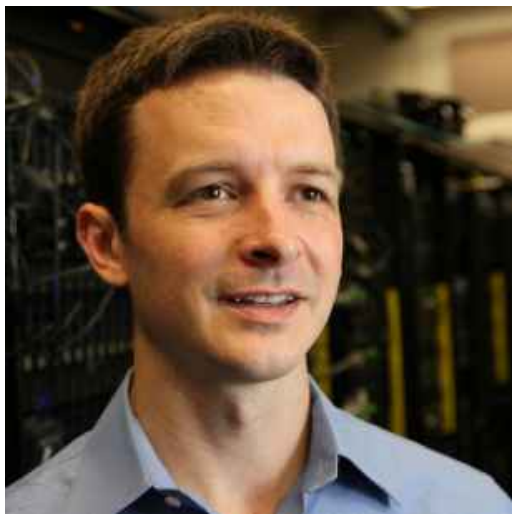
Acknowledgements



Tim Mueller

Neil Drummond

G. L. W. Hart and R. W. Forcade, Phys. Rev. B **77**, 224115 (2008)

Lattice, reciprocal lattice, and primitive cell

- Bravais lattice basis vectors $\mathbf{R}_{P_1}$, $\mathbf{R}_{P_2}$, and $\mathbf{R}_{P_3}$.
- Reciprocal lattice basis vectors $\mathbf{G}_{P_1}$, $\mathbf{G}_{P_2}$, and $\mathbf{G}_{P_3}$.
- $\mathbf{R}_{P_i} \cdot \mathbf{G}_{P_j} = 2\pi\,\delta_{ij}$.
- Primitive cell has volume $|\mathbf{R}_{P_1} \cdot (\mathbf{R}_{P_2} \times \mathbf{R}_{P_3})|$.
- First Brillouin Zone (BZ) has volume $|\mathbf{G}_{P_1} \cdot (\mathbf{G}_{P_2} \times \mathbf{G}_{P_3})|$.
- Change of basis:

$$\begin{aligned}
\mathbf{r}_{lmn} &= l\,\mathbf{R}_{P_1} + m\,\mathbf{R}_{P_2} + n\,\mathbf{R}_{P_3} \\
&= (l-n)\,\mathbf{R}_{P_1} + m\,\mathbf{R}_{P_2} + n\,(\mathbf{R}_{P_1} + \mathbf{R}_{P_3}) \\
&= l'\,\mathbf{R}'_{P_1} + m'\,\mathbf{R}'_{P_2} + n'\,\mathbf{R}'_{P_3} \\
&= \mathbf{r}_{l'm'n'}
\end{aligned}$$

- Same lattice, different basis vectors.

Superlattice basis vectors

- We construct the basis vectors of a superlattice by taking linear combinations of the basis vectors of the underlying parent lattice with integer coefficients.

$$\mathbf{R}_{S_1} = S_{11}\mathbf{R}_{P_1} + S_{12}\mathbf{R}_{P_2} + S_{13}\mathbf{R}_{P_3}$$
$$\mathbf{R}_{S_2} = S_{21}\mathbf{R}_{P_1} + S_{22}\mathbf{R}_{P_2} + S_{23}\mathbf{R}_{P_3}$$
$$\mathbf{R}_{S_3} = S_{31}\mathbf{R}_{P_1} + S_{32}\mathbf{R}_{P_2} + S_{33}\mathbf{R}_{P_3}$$

$$\begin{pmatrix} \mathbf{R}_{S_1} \\ \mathbf{R}_{S_2} \\ \mathbf{R}_{S_3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{R}_{P_1} \\ \mathbf{R}_{P_2} \\ \mathbf{R}_{P_3} \end{pmatrix}$$

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

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

Supercells in electronic structure calculations

- Used in conjunction with periodic boundary conditions.
- DFT - single-particle method.
  - Defects.
  - Finite displacement calculations of phonons.
- QMC - many-particle method.
  - Need to use a supercell in order to accurately describe long-range inter-particle correlation.
  - Use single particle orbitals generated on a k-point grid that is commensurate with the supercell to construct the Slater determinant.
- In QMC calculations the Jastrow factor is cutoff at half the distance between a particle and its nearest periodic image in order to prevent the introduction of delta functions into the local kinetic energy.

Hermite normal form (HNF)

- Two different supercell matrices S and S' generate different bases for the same superlattice if S' can be reduced to S by integer row operations.
- The canonical form for such operations is the upper-triangular HNF:

$$\begin{pmatrix} a & b & d \\ 0 & c & e \\ 0 & 0 & f \end{pmatrix}, \quad 0 \leq b < c\,, \quad 0 \leq d, e < f\,.$$

- Therefore we only search over supercell matrices S that are in HNF.
- Note that most electronic structure calculations using supercells are currently carried out with $b = d = e = 0$.

Let the search begin

- HNF:
$$\begin{pmatrix} a & b & d \\ 0 & c & e \\ 0 & 0 & f \end{pmatrix}, \quad 0 \leq b < c\,, \quad 0 \leq d, e < f\,.$$
- The product $a \times c \times f$ fixes the determinant $|S|$ and therefore the number of primitive cells contained within the supercell.
- Generating all HNF matrices with a given $|S|$ can be done by finding each unique triplet acf and then generating all values of b, d, and e that obey the conditions stated above.
- For each HNF matrix that is generated we calculate the radius of the largest sphere that can be inscribed in the Wigner-Seitz cell which is half the distance between a particle and its nearest periodic image.
- For our purposes, the optimal supercell is the one with the largest Wigner-Seitz cell radius.

Examples

- P21/c-24 is a candidate structure for phase II of solid hydrogen. At 100 GPa the lattice vectors (in Bohr) are:

$$\begin{aligned}\mathbf{R}_{P_1} &= 16.92312\,\hat{\mathbf{x}} + 0.004564\,\hat{\mathbf{z}} \\ \mathbf{R}_{P_2} &= 3.574513\,\hat{\mathbf{y}} \\ \mathbf{R}_{P_3} &= -11.28396\,\hat{\mathbf{x}} + 6.166606\,\hat{\mathbf{z}}\end{aligned}$$

$\lvert S\rvert$	Largest diagonal supercell radius	Largest possible supercell radius	% increase
2	3.574513	3.574513	0.00
4	4.179816	5.499818	31.58
8	6.783887	7.356347	8.44
16	7.149025	9.425474	31.84
32	8.461560	12.23685	44.62

More examples

- C2/c-24 is a candidate structure for phase III of solid hydrogen. At 200 GPa the lattice vectors (in Bohr) are:

$$\begin{aligned}
\mathbf{R}_{P_1} &= 2.831959\,\hat{\mathbf{x}} + 0.001245\,\hat{\mathbf{y}} - 4.896124\,\hat{\mathbf{z}} \\
\mathbf{R}_{P_2} &= -0.027137\,\hat{\mathbf{x}} + 10.05304\,\hat{\mathbf{y}} \\
\mathbf{R}_{P_3} &= 2.831959\,\hat{\mathbf{x}} + 0.001245\,\hat{\mathbf{y}} + 4.896124\,\hat{\mathbf{z}}
\end{aligned}$$

$\lvert S\rvert$	Largest diagonal supercell radius	Largest possible supercell radius	% increase
2	2.828075	2.831959	0.14
4	5.026538	5.656149	12.53
8	5.656149	7.016988	24.06
16	5.656149	9.010517	59.30
32	10.05308	11.32784	12.68

Reciprocal superlattice vectors

$$\begin{pmatrix} \mathbf{G}_{P_1} \\ \mathbf{G}_{P_2} \\ \mathbf{G}_{P_3} \end{pmatrix} = 2\pi \begin{pmatrix} \mathbf{R}_{P_1} \\ \mathbf{R}_{P_2} \\ \mathbf{R}_{P_3} \end{pmatrix}^{-\mathsf{T}}$$

$$\begin{pmatrix} \mathbf{G}_{S_1} \\ \mathbf{G}_{S_2} \\ \mathbf{G}_{S_3} \end{pmatrix} = \begin{pmatrix} \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{13} \\ \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{23} \\ \bar{S}_{31} & \bar{S}_{32} & \bar{S}_{33} \end{pmatrix} \begin{pmatrix} \mathbf{G}_{P_1} \\ \mathbf{G}_{P_2} \\ \mathbf{G}_{P_3} \end{pmatrix}$$

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

- The k-points that are commensurate with the supercell are those points on the reciprocal superlattice that lie within the first BZ of the parent reciprocal lattice.
- It is convenient to express these k-points in terms of the parent reciprocal lattice basis vectors.

Commensurate k-points

$$
\begin{aligned}
\mathbf{k}_{lmn} &= \begin{pmatrix} l & m & n \end{pmatrix} \begin{pmatrix} \mathbf{G}_{S_1} \\ \mathbf{G}_{S_2} \\ \mathbf{G}_{S_3} \end{pmatrix} \\
&= \begin{pmatrix} l & m & n \end{pmatrix} \begin{pmatrix} \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{13} \\ \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{23} \\ \bar{S}_{31} & \bar{S}_{32} & \bar{S}_{33} \end{pmatrix} \begin{pmatrix} \mathbf{G}_{P_1} \\ \mathbf{G}_{P_2} \\ \mathbf{G}_{P_3} \end{pmatrix} \\
&= \begin{pmatrix} l' & m' & n' \end{pmatrix} \begin{pmatrix} \mathbf{G}_{P_1} \\ \mathbf{G}_{P_2} \\ \mathbf{G}_{P_3} \end{pmatrix} \\
&= \mathbf{k}_{l'm'n'}
\end{aligned}
$$

- We refer to l', m', and n' as the fractional k-point coordinates. There are $|S|$ points on the reciprocal superlattice that lie within the first BZ of the parent reciprocal lattice.

Summary

- Superlattice vectors are defined by a supercell matrix S.
- Two different supercell matrices S and S' generate different bases for the same superlattice if S' can be reduced to S by integer row operations.
- Therefore we only search over supercell matrices S that are in Hermite Normal Form and for each one calculate the radius of the largest sphere that can be inscribed in the Wigner-Seitz cell.
- The optimal supercell is the one with the largest Wigner-Seitz cell radius.
- Open question - how much difference does choosing supercells in this way actually make?