The search for the optimal supercell

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Acknowledgements

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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:

  $$\mathbf{r}_{lmn} = l \mathbf{R}_P^1 + m \mathbf{R}_P^2 + n \mathbf{R}_P^3$$
  $$= (l - n) \mathbf{R}_P^1 + m \mathbf{R}_P^2 + n (\mathbf{R}_P^1 + \mathbf{R}_P^3)$$
  $$= l' \mathbf{R}'_P^1 + m' \mathbf{R}'_P^2 + n' \mathbf{R}'_P^3$$
  $$= \mathbf{r}_{l'm'n'}$$

- 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.

\[
\begin{align*}
\mathbf{R}_{S_1} &= S_{11} \mathbf{R}_{P_1} + S_{12} \mathbf{R}_{P_2} + S_{13} \mathbf{R}_{P_3} \\
\mathbf{R}_{S_2} &= S_{21} \mathbf{R}_{P_1} + S_{22} \mathbf{R}_{P_2} + S_{23} \mathbf{R}_{P_3} \\
\mathbf{R}_{S_3} &= S_{31} \mathbf{R}_{P_1} + S_{32} \mathbf{R}_{P_2} + S_{33} \mathbf{R}_{P_3}
\end{align*}
\]

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

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

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 $b = d = e = 0$. 

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

\[
\begin{align*}
R_{P_1} &= 16.92312 \hat{x} + 0.004564 \hat{z} \\
R_{P_2} &= 3.574513 \hat{y} \\
R_{P_3} &= -11.28396 \hat{x} + 6.166606 \hat{z}
\end{align*}
\]

| \(|S|\) | 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

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

\[
\mathbf{R}_{P_1} = 2.831959 \hat{x} + 0.001245 \hat{y} - 4.896124 \hat{z}
\]
\[
\mathbf{R}_{P_2} = -0.027137 \hat{x} + 10.05304 \hat{y}
\]
\[
\mathbf{R}_{P_3} = 2.831959 \hat{x} + 0.001245 \hat{y} + 4.896124 \hat{z}
\]

| \(|S|\) | 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

\[
\begin{pmatrix}
G_{P_1} \\
G_{P_2} \\
G_{P_3}
\end{pmatrix}
= 2\pi
\begin{pmatrix}
R_{P_1} \\
R_{P_2} \\
R_{P_3}
\end{pmatrix}^{-T}
\]

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

\[
\bar{S}_{ij} = S^{-1}_{ji}
\]

- 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

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

- 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.
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?