Phonon Dispersion

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We wish to calculate the phonon dispersion curve of solid p-H_2, which has hcp structure.

$(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ is a set of linearly independent primitive lattice vectors, such that any lattice point can be expressed as an integer linear combinations of them

$$\mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \tag{1}$$

where

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \tag{2}$$

$$\mathbf{a}_2 = \frac{a}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}a}{2}\hat{\mathbf{y}} \tag{3}$$

$$\mathbf{a}_3 = 2\sqrt{\frac{2}{3}}a\hat{\mathbf{z}} \tag{4}$$

any point in the reciprocal lattice can be written as the integer linear combination of reciprocal lattice vectors

$$\mathbf{G}_m = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \tag{5}$$

where

$$\mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a}\left(\sqrt{3}\hat{\mathbf{k}}_x - \hat{\mathbf{k}}_y\right) \tag{6}$$

$$\mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{\mathbf{k}}_y \tag{7}$$

$$\mathbf{b}_3 = \sqrt{\frac{3}{2}}\frac{\pi}{a}\hat{\mathbf{k}}_z \tag{8}$$

which satisfy

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \tag{9}$$

we shall work with primitive unit cell, which only contains one lattice point by definition, within each unit cell, we place the hydrogen molecules, which are labeled by κ, which only runs from 1 to 2 in our case of crystal hydrogen.

Where the two molecule basis are placed on the lattice point $(0, 0, 0)$ and in the center of the equilateral triangle formed by the 3 molecules in the layer above and below $(1/3, 1/3, 1/2)$.

The equilibrium position of the molecule with in the unit cell relative to lattice point is described by $\mathbf{r}_\kappa$.

Thermal motion will cause the molecules to be displaced from their equilibrium by $\mathbf{u}_{l\kappa}$, so that the total position of an molecule is given by

$$\mathbf{R}_{l\kappa} = \mathbf{R}_l + \mathbf{r}_\kappa + \mathbf{u}_{l\kappa} = \mathbf{R}^0_{l\kappa} + \mathbf{u}_{l\kappa} \tag{10}$$

given a potential energy surface V, the force constant matrix is given by

$$\Phi_{l\kappa\alpha,l'\kappa'\alpha'} = \frac{\partial^2 V}{\partial u_{l\kappa\alpha}\partial u_{l'\kappa'\alpha'}} \tag{11}$$

the dynamical matrix is defined as

$$D_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{l'} \Phi_{0\kappa\alpha,l'\kappa'\alpha'} e^{i\mathbf{q}\cdot(\mathbf{R}^0_{l'\kappa'} - \mathbf{R}^0_{0\kappa})} \tag{12}$$

the number of lattice points we sum over should be far enough so that the intermolecular interaction falls off and molecule should not interact with its own periodic image.

Phonon dispersion $\omega_{\mathbf{q}\nu}$ and normal modes $W_{\kappa\alpha}(\mathbf{q}\nu)$ are obtained by solving the eigenvalue equation

$$\sum_{\kappa'\alpha'} D_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) W_{\kappa'\alpha'}(\mathbf{q}\nu) = \omega^2_{\mathbf{q}\nu} W_{\kappa\alpha}(\mathbf{q}\nu) \tag{13}$$

where ν is a branch index $\mathbf{q}$ is a wave vector.

Thus, we need to diagonalise a 6×6 matrix along our chosen path in the Brillouin zone.

In practice, the force constant matrix is calculate by finite displacement

$$\Phi_{0\kappa\alpha,l'\kappa'\alpha'} = -\frac{\partial F_{0\kappa\alpha}}{\partial u_{l'\kappa'\alpha'}} \approx -\frac{F^+_{0\kappa\alpha} - F^-_{0\kappa\alpha}}{2\epsilon_{l'\kappa'\alpha'}} \tag{14}$$

where $F^{+/-}$ are the forces felt by the molecules in $l = 0$ cell due to small positive and negative displacement ϵ.

We choose the following path in reciprocal space of HCP lattice to construct the dispersion curve

$$\Gamma(0,0,0) \xrightarrow{\Lambda} K(2/3,1/3,0) \xrightarrow{T} M(1/2,0,0) \xrightarrow{\Sigma} \Gamma \xrightarrow{\Delta} A(0,0,1/2) \tag{15}$$

where the lines connecting the high symmetry points are

$$\Lambda(2\nu,\nu,0), \quad \nu : 0 \to \frac{1}{3} \tag{16}$$

$$T(1/2+\nu/2,\nu,0), \quad \nu : \frac{1}{3} \to 0 \tag{17}$$

$$\Sigma(u,0,0), \quad u : \frac{1}{2} \to 0 \tag{18}$$

$$\Delta(0,0,w), \quad w : 0 \to \frac{1}{2} \tag{19}$$

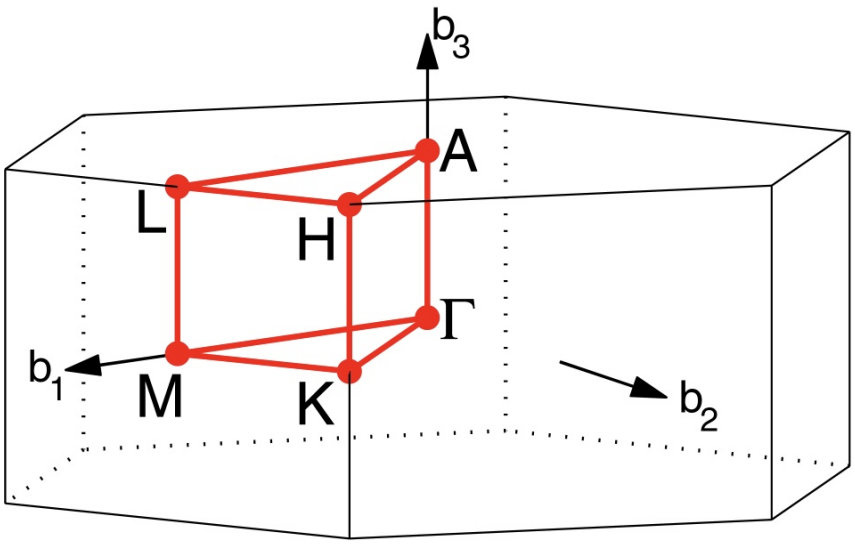

Figure 1: Brillouin zone of HCP lattice