Stability and superconductivity of lanthanum and yttrium decahydrides

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Rare-earth hydrides can exhibit high-temperature superconductivity under high pressure. Here, we apply a crystal structure prediction method to the current record-holding $T_c$ material, LaH$_{10}$, and a candidate for even higher $T_c$, YH$_{10}$. We find a pressure-induced phase transition from the experimentally observed cubic LaH$_{10}$ phase to a new hexagonal phase at around 420 GPa. This hexagonal phase could explain experimental observations of hcp impurities in fcc samples. We find that YH$_{10}$ forms similar structures to LaH$_{10}$ and discuss the sensitivity of superconductivity calculations to the computational parameters used.

I. INTRODUCTION

Hydrogen was predicted to be a room-temperature superconductor at very high pressure in 1968 [1], but the pressures required to metallise hydrogen are difficult to obtain. Hydrides have been suggested to have lower metallisation pressures than pure hydrogen due to chemical pre-compression [2] and therefore might become superconducting at more readily accessible pressures. This idea has motivated a surge of research examining potential superconductivity in high-pressure hydrides. There are several reviews summarising recent developments in this field [3–9].

Theoretical studies of ScH$_3$, LaH$_3$, [10], YH$_3$, YH$_4$ and YH$_6$ [11][13] identified hydrides of rare-earth elements as potential high-temperature superconductors. First-principles structure searching studies of rare-earth hydrides have reported structures with high hydrogen content adopting clathrate (cage-like) structures [14][15]. Of particular note, a phase to a new hexagonal phase at around 420 GPa. Slight distortions of the cubic LaH$_{10}$ phase were found to lead to C2/m and R3m structures at lower pressures [16][17], though Ref. [18] showed that quantum effects render $Fm3m$ as the true ground state.

These predictions were followed by experimental measurement of critical temperatures reaching 260 K in LaH$_{10}$ at 170-200 GPa [19][20]. These record-breaking measurements built on previous successful studies of superconductivity in H$_3$S [21][22]. The high-$T_c$ phase was determined to be a structure with an fcc arrangement of La atoms, giving support to theoretical predictions.

In addition to the aforementioned studies of lanthanum, scandium and yttrium hydrides, many other studies have also focused on rare-earth elements, exploring the synthesis and superconducting properties of cerium [23][24], praseodymium [25] and neodymium [26] hydrides. Here, within the framework of density functional theory (DFT) [27][28], we revisit LaH$_{10}$ and YH$_{10}$ using crystal structure prediction methods. We find a phase transition to a new hexagonal phase in LaH$_{10}$, potentially explaining experimental observations of hcp impurities in fcc samples [20]. We go on to predict the phases and corresponding critical temperatures that may be observed in YH$_{10}$.

II. THEORY AND METHODOLOGY

A. Phonons and superconductivity

The Hamiltonian of a coupled electron-phonon system can be written [29] as

$$ H = \sum_{k\phi} \epsilon_{nk} c_{nk}^\dagger c_{nk} + \sum_{q\nu} \omega_{q\nu} \left( a_{q\nu} a_{q\nu}^\dagger + \frac{1}{2} \right) + \frac{1}{\sqrt{N_p}} \sum_{k,m,n} g_{mn\nu}^q(k,\nu)c_{m,k+q\nu}^\dagger c_{nk} \left( a_{q\nu} + a_{-q\nu}^\dagger \right)$$

In this work, we calculate the electronic Kohn-Sham eigenvalues $\epsilon_{nk}$, phonon frequencies $\omega_{q\nu}$, and electron-phonon coupling constants $g_{mn\nu}^q(k,\nu)$ appearing in $H$ from first-principles using the QUANTUM ESPRESSO DFT code [30][31], which we optimised for this work [32]. The Hamiltonian in Eq. [14] can be treated within Migdal-Eliashberg theory [33], allowing us to define the electron-
boson spectral function

\[
\alpha^2 F(\omega) = \frac{1}{N(\epsilon_F)} \sum_{mnqv} \delta(\omega - \omega_{qv}) \sum_k |g_{mn}(k,q)|^2 \\
\times \delta(\epsilon_{m,k+q} - \epsilon_F) \delta(\epsilon_{n,k} - \epsilon_F).
\]

From \(\alpha^2 F\) we extract the superconducting critical temperature by solution of the Eliashberg equations using the ELK code [34]. Using the quantities appearing in \(H\) we may also construct the electronic and vibrational densities of states, from which we can derive the Gibbs free energy as a function of temperature. We do this at a range of pressures, allowing us to construct a pressure-temperature phase diagram.

To evaluate the double-delta sum in Eq. 2 for finite \(k\)- and \(q\)-point grids, we follow the method detailed in Appendix A of Ref. [35] and smear the delta functions with finite-width Gaussians. In order to best approximate the delta functions, the smallest sensible smearing should be used. However, the smearing must be large enough to accommodate the finite \(k\)-point grids used. We identify the optimal choice of smearing from discrepancies in the results between different \(k\)-point grids [35], as can be seen in Figs. 1 and 2.

Our electron-phonon calculations were carried out using the Perdew-Burke-Ernzerhof (PBE) generalised gradient approximation [46] and ultrasoft pseudopotentials, which were validated using the all-electron WIEN2k code [34]. Well-converged \(k\)-point grids with a spacing of at most \(2\pi \times 0.015 \text{ Å}^{-1}\) and an 820 eV plane wave cut-off were used [29]. The \(q\)-point grids used were typically 8 times smaller than the \(k\)-point grids and were Fourier interpolated to 10 times their original size. For the cubic systems studied, this corresponds to \(24 \times 24 \times 24\) \(k\)-point grids and a \(3 \times 3 \times 3\) \(q\)-point grid Fourier interpolated to \(30 \times 30 \times 30\).

B. Structure searching

Our structure searching calculations were performed using \textit{ab initio} random structure searching (AIRSS) [8, 40] and the plane wave pseudopotential code CASTEP [41]. The PBE functional, CASTEP QC5 pseudopotentials, a 400 eV plane wave cut-off and a \(k\)-point spacing of \(2\pi \times 0.05 \text{ Å}^{-1}\) were used in all searches.

III. RESULTS AND DISCUSSION

In the following sections, we report results in terms of phonon-corrected pressures, obtained by fitting the Birch-Murnaghan equation of state [42] to our data. Where DFT pressures are reported instead, they are labelled as \(P_{DFT}\) - this second set of pressures facilitates comparison with previous calculations as they are simply an input parameter to the DFT geometry optimisation.

A. LaH\(_{10}\)

Low enthalpy candidates found by AIRSS for LaH\(_{10}\) include the space groups \(Fn3m, R3m\), and a 2-formula-unit \(C2/m\), which had been identified previously. The searches also revealed a new structure of \(P6_3/mmc\) symmetry. These structures are shown in Fig. 3. A \(C2/m\) structure with 3 formula units per unit cell was also found to be energetically competitive, but was not considered further in this work as it behaves similarly to the 2-formula unit phase over the pressure range of interest.

The calculated LaH\(_{10}\) phase behaviour is shown in Fig. 4 and the corresponding critical temperatures are shown in Fig. 5. Our calculations for the \(Fn3m\) phase include
unstable phonon modes for $P_{\text{DFT}} \leq 210$ GPa. In the harmonic picture, explicitly taking into account this dynamical instability leads to a window of stability for the $C2/m$ phase [29], which is in agreement with previous calculations [16, 17]. However, we note that under the assumption that the unstable modes can be neglected in the calculation of the Gibbs free energy, we obtain the same behaviour as the anharmonic calculations of Ref. [18]. $Fm\overline{3}m$ is the only phase with a predicted region of stability at lower pressures. As the pressure increases, the $R\overline{3}m$ structure approaches $Fm\overline{3}m$ symmetry. This has been noted in previous theoretical work [18]. We therefore expect that these phases will not be distinguishable at high pressures.

At 300 K, the $P6_3/mmc$ structure becomes thermodynamically favourable for pressures above $\sim 420$ GPa. The existence of this new hexagonal phase could provide an explanation for the experimental observation of two kinds of hcp impurities in fcc-LaH$_{10}$ samples in Ref. [20]. We calculate $T_c = 232-259$ K for $Fm\overline{3}m$-LaH$_{10}$ at 269 GPa ($P_{\text{DFT}}=250$ GPa), which is lower than the previous theoretical result of $T_c = 257-274$ K [14]. However, we observe an increase in $T_c$ on reduction of the double-delta smearing parameter to below our calculated optimal value [29], potentially explaining this discrepancy. Careful choice of smearing has previously been noted to be important in other hydride systems [43]. We note a previous calculation of $T_c = 288$ K at 200 GPa [15], however, in agreement with other calculations [16, 17] we find $Fm\overline{3}m$ is dynamically unstable at this pressure. This dynamical instability means we cannot directly compare with experiment, which found $T_c = 250$ K at around 170 GPa [20] and $T_c = 260$ K at 180-200 GPa [19]. For the $C2/m$ phase, using an optimal value of smearing we calculate $T_c = 205-225$ K at 262 GPa ($P_{\text{DFT}}=250$ GPa), compared to $T_c = 229-245$ K in Ref. [17].

B. YH$_{10}$

Low-enthalpy candidates for YH$_{10}$ found using AIRSS include $Fm\overline{3}m$, which had been identified previously, a slight distortion of this phase, $R\overline{3}m$, and structures of $P6_3/mmc$ and $Cmcm$ symmetry. These structures are shown in Fig. 6. The calculated YH$_{10}$ phase behaviour is
FIG. 6. Structures of YH$_{10}$. (a) 2 formula unit/cell Cmcm, (b) 1 formula unit/cell Fm$ar{3}$m, (c) 2 formula unit/cell P6$_3$/mmc. The R$ar{3}$m structure is not shown as it is visually indistinguishable from the Fm$ar{3}$m structure at the pressures of interest.

shown in Fig. 7 and the corresponding critical temperatures are shown in Fig. 8. We do not claim to observe any phase transitions within the predicted range of stability of the YH$_{10}$ stoichiometry [15]. However, the difference in Gibbs free energy between the Fm$ar{3}$m and R$ar{3}$m phases is exceedingly small (see Fig. 7), reflecting their structural similarity.

Previous calculations for Fm$ar{3}$m found $T_c = 305-326$ K at 250 GPa [14] and $T_c = 303$ K at 400 GPa [15]. Here, we calculate $T_c = 270-302$ K at 324 GPa ($P_{DFT}=300$ GPa) and $T_c = 250-280$ K at 425 GPa ($P_{DFT}=400$ GPa). Our more conservative $T_c$ results can again be explained by considering the smearing parameter used to approximate the double-delta integral in Eq. 2. We were able to reproduce the results of previous calculations by using the minimum default smearing employed in QUANTUM ESPRESSO, which in this case overestimates $T_c$ by ~30 K (see Fig. 1) compared to optimal smearing. We note that our results agree with those obtained using Wannier interpolation techniques, which avoid the need for a smearing parameter entirely [13]. Using the same method to calculate an optimal smearing also provides results in agreement with recent experimental measurements for 1m$ar{3}$m-YH$_6$ [8], as shown in Fig. 2.

IV. CONCLUSIONS

We have identified a new hexagonal phase of LaH$_{10}$ with P6$_3$/mmc symmetry. Our calculations show a pressure-induced phase transition into this new phase from the cubic phase believed to be observed in experiment [19, 20]. The overall phase behaviour predicted within the harmonic picture is $C2/m \rightarrow Fm\bar{3}m \rightarrow P6_3/mmc$ with all three of these phases predicted to be high-$T_c$ superconductors; within their ranges of stability, $T^\text{max}_c$ is given by ~170 K, 250 K and 145 K, respectively. Making the assumption that unstable modes can be neglected, however, gives the same picture as in Ref. [18] where Fm$ar{3}$m is the true ground state at lower pressures. The existence of a new hexagonal phase could explain the observation of hcp impurities in recent experiments [20].

We found that YH$_{10}$ adopts very similar structures to LaH$_{10}$, with one of P6$_3$/mmc symmetry once again amongst the most energetically competitive candidates. Over the pressure range considered the Fm$ar{3}$m/R$ar{3}$m phase remains the most stable. The difference in Gibbs free energy between these two structures is extremely small, meaning synthesis of a pure sample of either of

FIG. 7. The Gibbs free energy as a function of pressure for energetically competitive phases of YH$_{10}$, plotted and interpolated relative to a third-order Birch-Murnaghan fit of the Fm3m data. Solid lines are at 300 K, dashed lines are at 0 K.

FIG. 8. Calculated $T_c(P)$ for dynamically stable phases of YH$_{10}$ from direct solution of the Eliashberg equations.
them could be difficult.

We found the double-delta smearing employed in superconductivity calculations to be of particular importance. Its effect on calculated $T_c$ changes from system to system; in particular, in our calculations the default minimum smearing employed by quantum espresso overestimates $T_c$ for LaH$_{10}$ by $\sim$20 K and YH$_{10}$ by $\sim$30 K when compared to optimal smearing.

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FIG. 9. Pressure-volume curve calculated using the all-electron code WIEN2k compared to data obtained using CASTEP and QUANTUM ESPRESSO for $Fm\bar{3}m$ LaH$_{10}$. The WIEN2k data was calculated for Ref. [17] and was provided to us by Hanyu Liu.

SUPPLEMENTARY MATERIAL

V. PRESSURE-VOLUME CURVES

In order to validate the pseudopotentials used in QUANTUM ESPRESSO, we compared the pressure-volume curves produced for clathrate structures LaH$_{10}$ and YH$_6$ to data obtained using CASTEP - another density functional theory (DFT) pseudopotential code - and using the all-electron code WIEN2k [37]. Figs. 9 and 10 contain data points produced by the following codes and pseudopotentials:

- QUANTUM ESPRESSO [30, 31]: Scalar-relativistic, ultrasoft PBE pseudopotentials downloaded from [https://www.quantum-espresso.org/pseudopotentials/ps-library]

- CASTEP [41]: on-the-fly (OTF) pseudopotentials generated with default pseudopotential strings for hydrogen and yttrium and 2|2|3|5|6|7|50U:60:51:52:434f0.1(qc=4.5)[4f0.1] for lanthanum

Good agreement between QUANTUM ESPRESSO and WIEN2k is observed in both cases. The structure searches in this work used CASTEP QC5 pseudopotentials, instead of OTF pseudopotentials, for computational efficiency.

VI. STRUCTURE SEARCHING AND CONVEX HULLS

We constructed well-converged convex hulls for the La-H and Y-H systems using AIRSS [8, 40] and qhull [44], as illustrated in Figs. [11] and [12]. Our convex hulls confirm the findings of previous work showing that the LaH$_{10}$ and YH$_{10}$ stoichiometries are on or close to the hull over the pressure ranges we study here (~150-500 GPa for LaH$_{10}$ and >~300 GPa for YH$_{10}$) [15].

FIG. 11. An example convex hull for the La-H system, showing that LaH$_{10}$ is stable to decomposition (at the static lattice level) at 250 GPa.
FIG. 12. An example convex hull for the Y-H system, showing that \( YH_{10} \) is meta-stable (at the static lattice level) at 400 GPa. We note that our Y-H hull identifies the \( YH_4 \), \( YH_6 \) and \( YH_9 \) structures recently reported in experiment [38, 39] (\( I4/mmm, Im\bar{3}m \) and \( P6_3/mmc \), respectively), highlighting the success of crystal structure prediction methods.

Throughout this work, we found the c2x software extremely useful for converting between CASTEP and QUANTUM ESPRESSO file formats and reporting symmetries at various tolerances.

VII. DFT ENERGIES

Fig. 13 shows the relative energies of the \( LaH_{10} \) phases, neglecting phonon contributions. Fig. 14 shows the same for \( YH_{10} \) phases. The structure files for all structures studied in this work are available at https://doi.org/10.17863/CAM.46481.

VIII. CONVERGENCE TESTING

The first stage towards calculating accurate phase diagrams and superconducting critical temperatures is to establish the computational parameters required to achieve the desired accuracy. In this work, the most relevant parameters were

- Electronic plane-wave cutoff
- Electronic \( k \)-point sampling density
- Electronic occupation smearing width/scheme
- Phonon \( q \)-point sampling density

The electronic occupation smearing width was found to be of particular importance. It is important to note that this is the Fermi-surface smearing used during SCF convergence, not the smearing used to evaluate double-delta integrals in superconductivity theory. For typical DFT energy calculations the smearing of the electronic Fermi surface often makes a negligible difference, even with high effective temperatures. This is because the energy scale of the electronic band structure is typically equivalent to thousands of Kelvin, due to Fermi statistics pushing electrons into higher and higher energy states. As the total energies are only sensitive to the average change
in the occupied energy states, and because the smearing is symmetric around the Fermi surface, we can use high smearing temperatures when we are only interested in total energies. Unfortunately the same is not true for electron-phonon coupling parameters. Only states close to the Fermi surface contribute significantly to electron-phonon coupling. Therefore, in order to calculate accurate electron-phonon coupling properties, we need an accurate resolution of the (unsmear) Fermi surface. To describe a Fermi surface accurately, we therefore require good Brillouin zone resolution, which means large k-point grids. This can be seen in Fig. 15. The resulting parameter set for LaH$_{10}$ is a 60 Ry cutoff, a k-point grid with a spacing of $2\pi \times 0.015 \text{ Å}^{-1}$ (equivalent to a $24 \times 24 \times 24$ grid for the $Fm\bar{3}m$ phase) and a q-point grid that is 8 times smaller than the k-point grid (equivalent to a $3 \times 3 \times 3$ grid for the $Fm\bar{3}m$ phase). From Fig. 15 we see that the difference between using 300 K and 3000 K smearing leads to a greater error in $T_c$ than using an approximate $\mu^*$, but does not noticeably impact convergence; this allows us to use 300 K smearing without significant loss of efficiency. In order to carry out these calculations within a reasonable time-frame, we have optimised the electron-phonon coupling code in QUANTUM ESPRESSO, leading to a 10× speedup for our systems. These changes have been submitted (and accepted) to the QUANTUM ESPRESSO project to allow others to benefit from our modifications. Since the electron-phonon calculations require such high convergence parameters, thermodynamic quantities are already well-converged at the chosen parameters, as shown in Fig. 16 and 17.

**IX. TREATMENT OF DOUBLE-DELTA SMEARING**

As noted in the main text, we use a multiple-grid scheme to ensure that the double-delta smearing parameters used are appropriate. It is quite straightforward to see that below a certain smearing value strong discrepancies between different grid sizes arise; see Fig. 18 for example. We have modified our version of QUANTUM ESPRESSO so that we can increase the number of double-delta smearing values used, ensuring that we can always identify this region of insufficient smearing.

**X. BACKGROUND THEORY: ELECTRON-PHONON COUPLING IN DFT**

Typically, within DFT the nuclear coordinates, $R$, are treated as fixed and the electronic Kohn-Sham system is solved within the fixed nuclear potential. In order to calculate the effects of electron-phonon coupling from within the DFT formalism we must consider leading-order corrections to the Born-Oppenheimer approximation in nuclear displacements. Expanding our Kohn-Sham poten-
phonon coupling Hamiltonian in second-quantized form

$$V_{KS}(R + \delta R) = V_{KS}(R) + \sum_{\kappa,p} \frac{\partial V_{KS}}{\partial R_{\kappa,p}} \cdot \delta R_{\kappa,p} + O(\delta R^2).$$

where $R_{\kappa,p}$ is the position of atom $\kappa$ in unit cell $p$. An atomic displacement of an atom can be written in terms of phonon creation and annihilation operators as

$$\delta R_{\kappa,p} = \frac{1}{\sqrt{N_p M_{\kappa}}} \sum_{q_{\nu}} e^{iq \cdot R_{\kappa}} \frac{1}{\sqrt{2\omega_{\nu}}} \left( a_{q_{\nu}} + a_{q_{\nu}}^\dagger \right) e_{\kappa q}(q)$$

where $e_{\kappa q}(q)$ and $\omega_{q\nu}$ are, respectively, the eigenvector and frequency of the phonon mode with creation operator $a_{q_{\nu}}^\dagger$. $R_{\kappa}$ is the position of the $\kappa$th unit cell within the periodic cell, of which there are $N_p$. $M_{\kappa}$ is the mass of atom $\kappa$. Substituting this into Eq. [3] we obtain

$$V_{KS}(R + \delta R) = V_{KS}(R) + \frac{1}{\sqrt{N_p}} \sum_{q_{\nu}} G_{q_{\nu}} (a_{q_{\nu}} + a_{q_{\nu}}^\dagger)$$

where

$$G_{q_{\nu}} = \frac{1}{\sqrt{2\omega_{q_{\nu}}} \sqrt{M_{\kappa}}} \sum_{\kappa} e_{\kappa q}(q) \frac{\partial V_{KS}}{\partial R_{\kappa,p}}$$

This allows us to write down the resulting electron-phonon coupling Hamiltonian in second-quantized form as

$$H_{ep}(\delta R) = \sum_{\kappa n k' \nu} \langle n, k | V_{KS}(R + \delta R) - V_{KS}(R) | n', k' \rangle c_{\kappa n k'}^\dagger c_{\nu n k}$$

$$= \sum_{q_{\nu}} \left( \sum_{n k n' k'} \langle n, k | G_{q_{\nu}} | n', k' \rangle c_{\kappa n k'}^\dagger c_{\nu n k} \right) \frac{a_{q_{\nu}} + a_{q_{\nu}}^\dagger}{\sqrt{N_p}}$$

where $c_{\kappa n k'}^\dagger$ creates a Kohn-Sham electron in orbital $n$, wavevector $k$ (i.e. occupies the Bloch state $u_{n k}(x) \exp(ik \cdot x) / \sqrt{N_p}$). Substituting our definition of $G_{q_{\nu}}$ we have

$$\langle n, k | G_{q_{\nu}} | n', k' \rangle = \frac{1}{\sqrt{2\omega_{q_{\nu}}} \sqrt{M_{\kappa}}} \sum_{\kappa} e_{\kappa q}(q) \frac{\partial V_{KS}}{\partial R_{\kappa,p}} | n', k' \rangle$$

FIG. 15. Convergence properties for the critical temperature of the $Fm\bar{3}m$ phase of LaH$_{10}$ for different values of double-delta smearing $\sigma$. The blurred section around each line represents the distribution of $T_C$ for different values of the $\mu^*$ parameter.
FIG. 16. Convergence behaviour of phonon frequencies for \(Fm\bar{3}m\) LaH\(_{10}\). Each line corresponds to a different phonon mode.

FIG. 17. Convergence behaviour of Helmholtz free energies (including vibrational contributions) for \(Fm\bar{3}m\) LaH\(_{10}\). Different lines correspond to different temperatures.

FIG. 18. \(T_c\) vs. double-delta smearing for \(Fm\bar{3}m\) YH\(_{10}\), calculated using different sized k-point grids with a fixed \(3 \times 3 \times 3\) q-point grid.

FIG. 19. \(T_c\) vs. double-delta smearing for \(Fm\bar{3}m\) YH\(_{10}\), calculated using different sized q-point grids. The results for primary/auxiliary k-point grids for each q-point grid are shown (primary = 512 k-points per q-point, auxiliary = 261 k-points per q-point).
FIG. 20. $T_C$ vs. double-delta smearing for $Fm\bar{3}m$ LaH$_{10}$, calculated using different sized k-point grids with a fixed $3 \times 3 \times 3$ q-point grid.

Now

$$\langle n, k | \frac{\partial V_{KS}}{\partial R_{\kappa,p}} | n', k' \rangle$$

$$= \frac{1}{N_p} \int u_{n,k}^*(x)e^{-ik\cdot x} \frac{\partial V_{KS}}{\partial R_{\kappa,p}}(x)u_{n',k'}(x)e^{ik'\cdot x} \, dx$$

$$= \frac{1}{N_p} \int u_{n,k}^*(x-R_p)e^{-ik\cdot(x-R_p)} \frac{\partial V_{KS}}{\partial R_{\kappa,p}}(x-R_p)$$

$$\times u_{n',k'}(x-R_p)e^{ik'\cdot(x-R_p)} \, dx$$

$$= e^{iR_p \cdot (k-k')} \int_{\text{unit-cell}} u_{n,k}^*(x)e^{-ik\cdot x} \frac{\partial V_{KS}}{\partial R_{\kappa,0}}(x)u_{n',k'}(x)e^{ik'\cdot x} \, dx$$

where in the last line we have used Bloch’s theorem and the fact that

$$\frac{\partial V_{KS}}{\partial R_{\kappa,p}}(x-R_p) = \frac{\partial V_{KS}}{\partial R_{\kappa,0}}(x)$$

where $R_{\kappa,0}$ is the position of atom $\kappa$ in the first unit cell. We may now write Eq. [8] as

$$\langle n, k | G_{qv} | n', k' \rangle$$

$$= \frac{1}{\sqrt{2\omega_{qv}}} \sum_{\kappa} \frac{\epsilon_{\kappa}(q)}{\sqrt{M_\kappa}} \langle n, k | \frac{\partial V_{KS}}{\partial R_{\kappa,0}} | n', k' \rangle_{uc}$$

$$\times \sum_{p} e^{i(q+(k-k')\cdot R_p)} N_p \delta_{q-k}$$

where the subscript “uc” on the ket means integration only over the first unit cell. Finally we obtain the DFT electron-phonon coupling Hamiltonian

$$H_{ep} = \frac{1}{\sqrt{N_p}} \sum_{q,k,m,n} \langle m, k+q | G_{qv,uc} | n, k \rangle_{uc}$$

$$\times e^\dagger_{m,k+q}c_{n,k}(a_{qv} + a_{-qv}^\dagger)$$

where we have defined

$$G_{qv,uc} = \frac{1}{\sqrt{2\omega_{qv}}} \sum_{\kappa} \epsilon_{\kappa}(q) \frac{\partial V_{KS}}{\partial R_{\kappa,0}}$$

This allows us to write down the Hamiltonian for an interacting Kohn-Sham-electron-phonon system, correct to first order in electron-phonon coupling constants $g_{mn\nu}(k,q) = \langle m, k + q | G_{qv,uc} | n, k \rangle_{uc}$:

$$H = \sum_{kn} \epsilon_{n,k} c_{n,k}^\dagger c_{n,k} + \sum_{q
u} \omega_{q
u} \left( a_{q
u}^\dagger a_{q
u} + \frac{1}{2} \right) +$$

| Electronic dispersion | phonon dispersion |
|-----------------------|------------------|
| $\frac{1}{\sqrt{N_p}} \sum_{q
u} g_{mn\nu}(k,q) c_{m,k+q}^\dagger c_{n,k} (a_{q
u} + a_{-q
u}^\dagger)$ | $\lambda_{q,v} = \frac{1}{N(\epsilon_F)\omega_{q\nu}\Omega_{BZ}} \times \sum_{nm} \int_{BZ} |g_{mn\nu}(k,q)|^2 \delta(\epsilon_{n,k} - \epsilon_F) \delta(\epsilon_{m,k+q} - \epsilon_F) \, dk$ |

From the parameters in this Hamiltonian we can also define the electron-phonon coupling strength associated with each phonon mode, $\lambda_{q,v}$, and the isotropic Eliashberg spectral function, $\alpha^2 F(\omega)$

$$\lambda_{q,v} = \frac{1}{N(\epsilon_F)\omega_{q\nu}\Omega_{BZ}} \times \sum_{nm} \int_{BZ} |g_{mn\nu}(k,q)|^2 \delta(\epsilon_{n,k} - \epsilon_F) \delta(\epsilon_{m,k+q} - \epsilon_F) \, dk$$

$$\alpha^2 F(\omega) = \frac{1}{2\Omega_{BZ}} \sum_{\nu} \int_{BZ} \omega_{q\nu} \lambda_{q\nu} \delta(\omega - \omega_{q\nu}) \, dq$$

from which we may calculate the critical temperature by solution of the Eliashberg equations [33]. The only additional requirement is the Morel-Anderson pseudopotential [35], which we treat as an empirical parameter with values between 0.1 and 0.15.