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The Mechanical Compression Enhancement of Electronic Degeneracy in Superconducting Hydrides

Hang Hu,^{1, a)} Hsu Kiang (James) Ooi,¹⁾ and Anguang Hu²⁾

¹*Data Science for Complex systems, Digital Technologies Research Centre, National Research Council Canada, Ontario, K1A 0R6, Canada*

²*Suffield Research Centre, Defence Research Development Canada, Medicine Hat, AB T1A 8K6 Canada.*

^{a)} *Corresponding author: hang.hu@cnrc-nrc.gc.ca*

Abstract. As one of the fundamental phenomena in quantum mechanics, quantum degeneracy is a specific regime in which collective and coherent phenomena dominate. The Cooper pair of a metal superconductor is an example of quantum degeneracy. Therefore, it is imperative to understand the dynamic formation and breaking process of quantum degeneracy of high-temperature superconductors relevant to spatial dimension and symmetry constraints. We developed an accurate non-perturbation electron-phonon interaction simulation and applied it to study the dynamic process of removing electronic degeneracy in superconducting hydrides under mechanical compression. The simulation shows that the degenerate electronic energy levels near the Fermi surface may hold more electrons or holes to form Cooper pairs. However, the direct electron-phonon interactions related to specific vibrational motion can remove electronic degeneracy, breaking Cooper pairs even at absolute zero temperature. The specific vibrational motion to stretch chemical bonds can interact with Cooper pairs, spontaneously and dynamically removing all degeneracies. Combined with spatial dimension and symmetry constraints, mechanical compression can enhance the electronic degeneracy to keep Cooper pairs in superconducting hydrides. As a result, such simulations may apply to search for stable high-temperature superconducting hydrides at lower pressures.

INTRODUCTION

The interaction of electrons and phonons, the fundamental vibrations of atoms in crystal lattices, is a key to many material properties and phenomena, such as band structure distortion and phonon dispersion relations [1–3]. This interaction is also the key to lifting degenerate energy bands in solid-state materials. In quantum mechanics, states are degenerate if they share the same energy level [4]. From the molecular orbitals theory, orbitals degenerate due to equivalent chemical bonds in a symmetrical arrangement [4,5]. Since the source of degeneracy is often due to symmetry, for most systems, the degenerate energy level can be removed by breaking the symmetry [6,7]. For molecular systems, this is known as the Jahn-Teller effect, where spontaneous symmetry breaking of a molecule can separate degeneracy and lower the overall system energy [8]. It is known that symmetry breaking is driven by electronic interactions from atomic oscillations, resulting in phenomena such as superconductivity, Fermi-surface nesting, Peierls distortions, and cooperative Jahn-Teller effects in solids [9–13]. The theoretical approach to studying these phenomena relies on determining a broken symmetry [14–16]. However, current theory estimates that the energy requirement for broken symmetry states is high, generally in the range of thousands of meV, but broken symmetry ground states have been observed at very low-temperature ranges [17]. Another approach to resolving degenerate energy levels is with an external field. However, rather than relying on external stimuli, a phonon is an intrinsic source of vibration which can induce local or global electrical field disturbance [18].

In this contribution, we report detailed first-principle density functional theory (DFT) calculations of the electronic properties of different superconducting materials, including metals and hydrides. The simulations will demonstrate how the quantum states accumulation at high symmetry points in the momentum (\mathbf{k}) space and atomic phonon vibrations coordinates in the real space will affect the band structure energy level and lifting degeneracies.

METHODOLOGY

The crystal structures and electronic properties for all atoms are calculated using density-functional theory with a full-potential numerical-atomic-orbital (FP-NAO) basis set as implemented in the FHI-aims package [19]. Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used as the exchange-correlation functional [20]. For Nb the symmetry group is $IM\bar{3}M$, and for H₃S the crystal group is $IM\bar{3}M$ and for LaH₁₀ the crystal group is $FM\bar{3}M$. A $5 \times 5 \times 5$ K-point grid was adopted for all three previously mentioned cubic symmetry groups. Geometry optimization was assumed finished when the force on each atom is smaller than 0.005 eV/Å.

The equation for evaluating temperature-dependent band energy under the harmonic approximation is given as follows:

$$\varepsilon_{nk}(T) = \varepsilon_{nk}(0) + \sum_{q,v} \frac{1}{2\omega_{qv}} \frac{\partial^2 \varepsilon_{nk}}{\partial u_{qv}^2} \left[\frac{1}{2} + n_B(\omega_{qv}, T) \right] + O(u^4) \quad (1)$$

where ε_{nk} is band energy along a wave vector \mathbf{k} and n is the band index, T is temperature, \mathbf{k} is the wave vector, ω_{qv} is the frequency of vibration mode qv , u is the vibration coordinate, and n_B is the average number of this vibration mode, as given by the Bose-Einstein formula. Equations 2 and 3 are used to evaluate the first-order and second-order derivatives of electronic band energy with respect to vibrational mode coordinates.

$$\frac{\partial \varepsilon_{nk}}{\partial u_{qv}} \approx \frac{\varepsilon_{nk}(-2\Delta u_{qv}) - 8\varepsilon_{nk}(-\Delta u_{qv}) + 8\varepsilon_{nk}(\Delta u_{qv}) - \varepsilon_{nk}(2\Delta u_{qv})}{12\Delta u_{qv}} \quad (2)$$

$$\frac{\partial^2 \varepsilon_{nk}}{\partial u_{qv}^2} \approx \frac{-\varepsilon_{nk}(-2\Delta u_{qv}) + 16\varepsilon_{nk}(-\Delta u_{qv}) - 30\varepsilon_{nk}(0) + 16\varepsilon_{nk}(\Delta u_{qv}) + \varepsilon_{nk}(2\Delta u_{qv})}{12(\Delta u_{qv})^2} \quad (3)$$

While equations 2 and 3 represent numerical approach to evaluate the derivatives, the accuracy of this approach can be evaluated. We know the first-order derivative of band energies with respect to mode coordinate should be zero in the whole Brillouin zone. From our calculation results, all the first-order derivatives are zero up to 0.1 meV/Å. The second-order derivatives are generally not zero for the longitudinal modes with positive values suggesting an increase to the band energy level and the negative second-order derivatives indicate a decrease in the band energy level. This provides a unique opportunity to evaluate how electron-phonon interactions affect degenerate energy bands.

RESULTS AND DISCUSSION

The band structure of Nb is shown in Figure 1a. The band index is based on the number of total electrons within a unit cell. For Nb, bands 37 to 41 are the valence bands, and 42 to 43 are the conduction bands. Nb is a conductor with energy bands crossing the fermi level around symmetry points Γ , N, H, and P. The crystal structure of solids can have a large number of chemical bonds with similar energy levels repeating in pattern due to symmetry. In the k-space, this phenomenon can lead to an accumulation of electron states at the high symmetry points of a space group, creating degenerate energy bands. The second-order derivative results of the longitudinal phonons for Nb are shown in Figure 1b. For Figure 1b, we observed a series of mirrored peaks. The position of these mirrored peaks corresponds to points of degeneracy in the band structure. For example, bands 37 and 38 are degenerate at symmetry point H, and we observed mirrored peaks at the same symmetry point in Figure 1b. Similar behaviour was observed for 42-43, which are degenerate between symmetry points P and Γ . Generally, the conduction band peaks are higher than the valence band peaks. This makes sense since the conduction bands are at higher energy levels. As mentioned in the methodology section, positive second-order derivative values indicate increasing band energy, and vice versa for negative second-order derivatives. After combing through all the longitudinal phonon modes, we found mirrored peaks corresponding to every instance of degeneracies from the band structure calculation. This correlation indicates that electron-phonon interaction can naturally remove all the degeneracies by simultaneously shifting band energies.

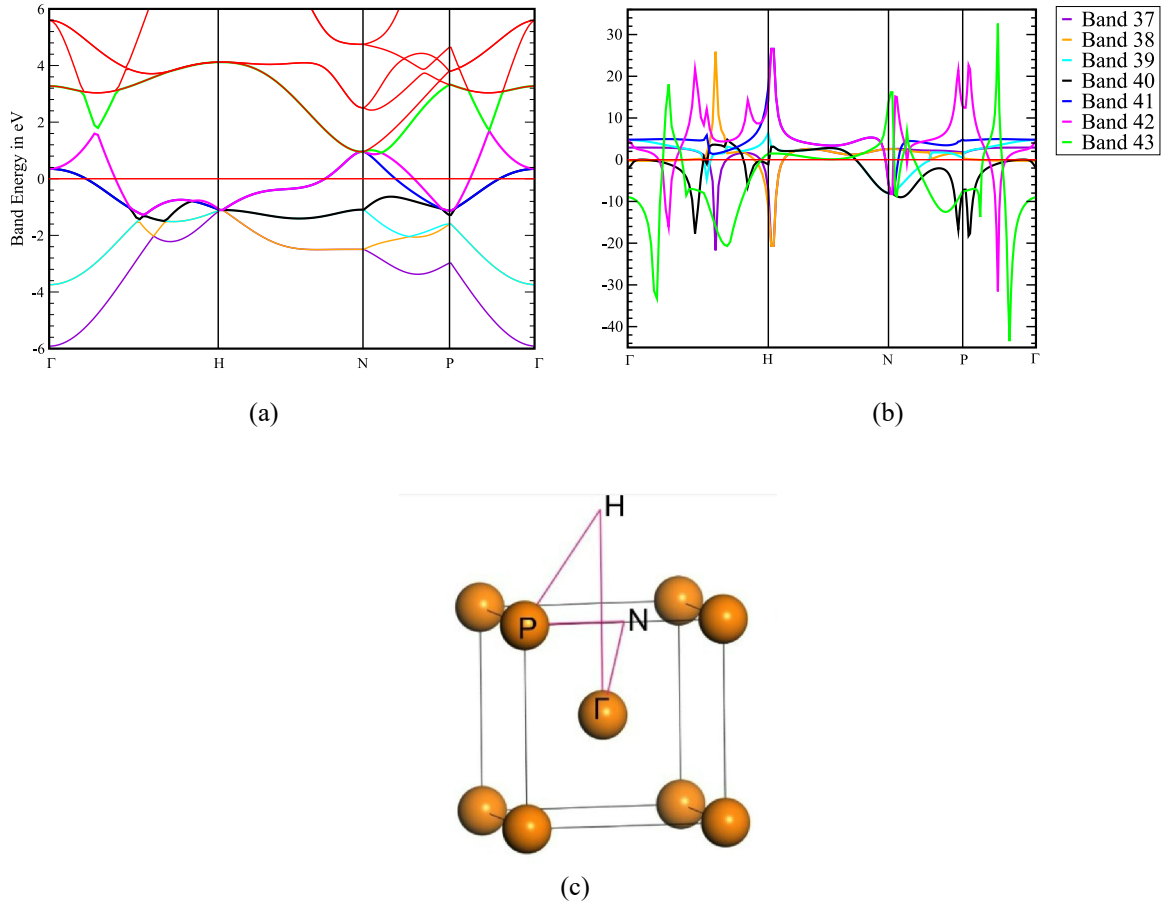


FIGURE 1. (a) Band structure of Nb crystal. (b) The second-order derivatives ($\text{eV}/\text{\AA}^2$) for the electron-phonon interaction of Nb with the lattice wave-vector $(0, 0, 0)$, corresponds to vibration frequency 292.21cm^{-1} . The red dashed line represents the fermi level. Band number 37 to 41 are the valence bands, and band number 42 and 43 are the conduction bands. (c) The Nb cubic structure and its symmetry points.

The figures for the other longitudinal modes are not included for brevity. It is worthwhile to look into the relationship between the symmetry point in the k -space and real space. The vibration patterns of phonon modes in Figure 1b correspond to bond stretching motion between a corner atom and the center atom in an Nb crystal. The Nb cubic structure and the real space location of the symmetry point are shown in Figure 1c. From symmetry point H and Γ is a line connecting the cube's center to the next cube's center. Symmetry points H to P represent a line between the center and the corner of the cube. Any bond stretching motion, regardless of axis, will induce electron-phonon interaction and register an intense peak in Figure 1b. Based on our calculation results, transverse modes with atomic vibrations parallel to the chemical bond have a smaller impact than longitudinal modes with atomic vibrations perpendicular to the bonds.

We observed a similar correlation between the mirrored peaks of the second-order derivative of band energy with respect to points of degeneracy for superconducting hydrides H_3S (Figure 2) and LaH_{10} (Figure 3). For H_3S at 200 GPa pressure, there are over 5 mirrored second-order derivative peaks between symmetry point Γ and H in Figure 2b, each corresponding to the point of degeneracy in Figure 2a. For LaH_{10} at 300 GPa pressure, there are several broader mirrored peaks along either side of symmetry point X for bands 32 and 33 in Figure 3b. In Figure 3a, bands 32 and 33 are degenerate at the same k -space location, agreeing with previous observations. The band structures show that mechanical compression can enhance electronic degeneracy for superconducting hydrides. We have previously pointed out that the presence of degenerate states is due to crystal symmetry. The accumulation of electron states at these degenerate states may facilitate the formation of more Cooper pairs. Under BCS theory, at the superconducting transition temperature (T_c), the thermal energy becomes sufficient to break a significant number of Cooper pairs. As more pairs are broken, the superconducting material loses its zero electrical resistance and other superconducting properties, returning to a normal conducting state. The potential breaking of Cooper pairs due to the

interaction with phonons is a key mechanism in understanding how superconductors transition from the superconducting phase to the normal phase as temperature increases. Our simulation results show that the electron-phonon interaction associated only with longitudinal vibration motion can lift the degeneracy and break the Cooper pairs even at very low temperatures. Therefore, the frozen longitudinal vibrational motion may maintain electron degeneracy and stabilize Cooper pairs to achieve superconductivity. Crystal structures with more electron degeneracy and intrinsic frozen longitudinal vibrational motion would be superconducting candidates.

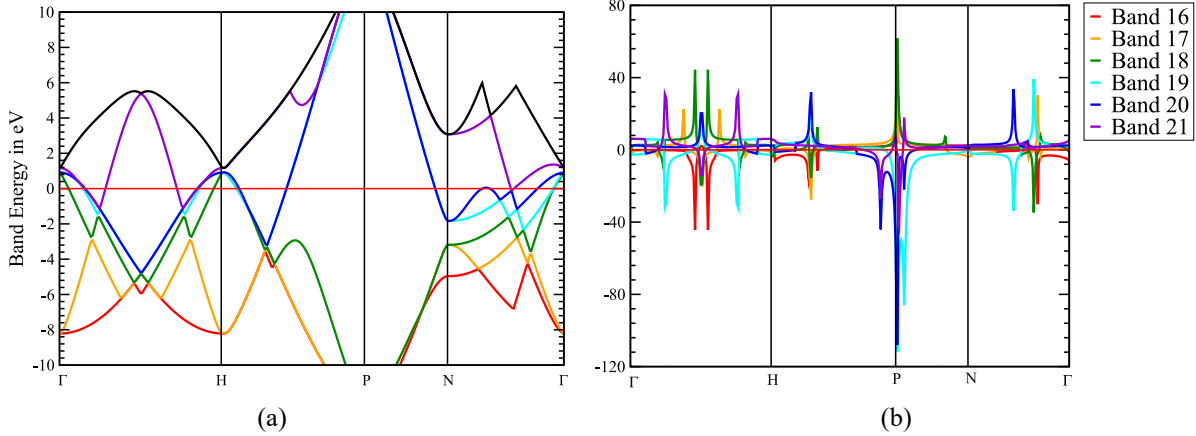


FIGURE 2. (a) Band structure of H₃S crystal at the 200 GPa pressure. (b) The second-order derivatives ($\text{eV}/\text{\AA}^2$) for the electron-phonon interaction of H₃S with the lattice wave-vector (0, 0, 0), corresponds to vibration frequency 292.21cm^{-1} . The red dashed line represents the fermi level. Band number 16 to 19 are the valence bands, and band number 20 and 21 are the conduction bands.

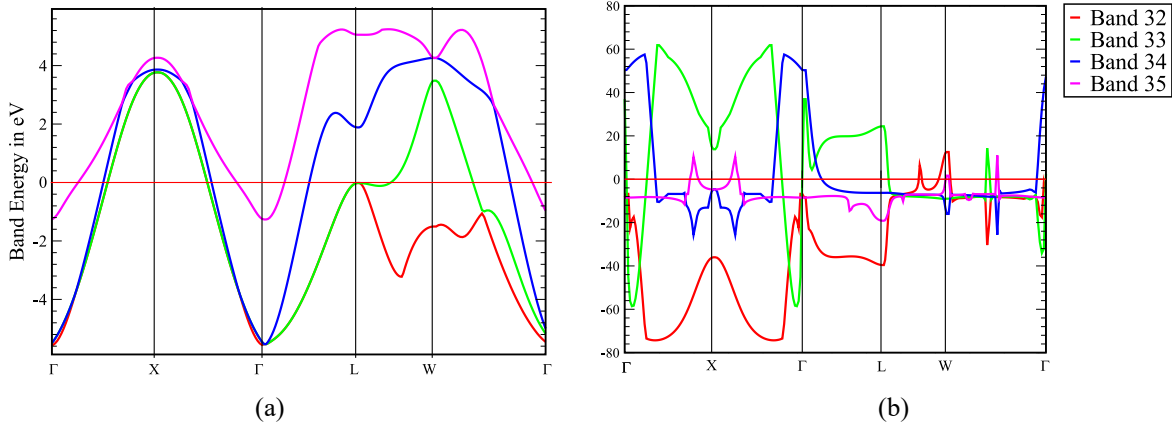


FIGURE 3. (a) Band structure of LaH₁₀ crystal at the 300 GPa pressure. (b) The second-order derivatives ($\text{eV}/\text{\AA}^2$) for the electron-phonon interaction of LaH₁₀ with the lattice wave-vector (0, 0, 0), corresponds to vibration frequency 1454.24cm^{-1} . The red dashed line represents the fermi level. Band number 32 to 34 are the valence bands, and band number 35 are the conduction bands.

CONCLUSION

This article reports on a novel computational study highlighting the close relationship between electron-phonon interaction and degeneracy lifting of energy bands. The simulation was carried out on superconducting material crystals belonging to different symmetry groups. For all the systems studied, if the **k-space** path between two high symmetry points followed a bond or had consistent spacing between nearby atoms in the real space, the energy bands

will exhibit consistent 2 to 4 degrees of degeneracy throughout the path. The second-order derivative of energy bands with respect to phonon vibrational coordinates provides a direct measurement of the strength of electron-phonon interactions. At every point or path of degeneracy in the calculated band structure, we observed corresponding mirrored second-order derivative peaks, naturally separating the degeneracies. Generally, the peaks for bands with larger band indexes are higher than those with smaller ones. The intensity of the peaks depends on the accumulation of electron states at a symmetry point and the direction of atomic vibrational motion. By identifying the role of phonon mode in degeneracy lifting, we can open a new vista to explore the impact of electron-vibration interactions on the breaking of Cooper pair at very low-temperature conditions.

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