

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**CHARGE DENSITY WAVES IN TRANSITION METAL
DI-CHALCOGENIDES:
A COMPARISON OF FERMI SURFACE NESTING
AND ELECTRON-PHONON COUPLING**

M.Sc. THESIS

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Department of Physics Engineering

Physics Engineering Programme

MAY 2024

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**GEÇİŞ METALLİ Dİ-KALKOJENLERDE YÜK YOĞUNLUK DALGALARI:
FERMİ YÜZEYİ YUVALANMASI VE ELEKTRON-FONON
ETKİLEŞİMİ'NİN KARŞILAŞTIRILMASI**

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Date of Submission : 24 April 2024

Date of Defense : 16 May 2024



To my family and friends,





FOREWORD

Firstly, I would like to express my sincere gratitude to my advisor Prof. Dr. Tuğrul Hakioglu for the continuous support of my study, his patience, motivation, and immense knowledge. His support and guidance helped me all the time in my study. He constantly pushed me forward to improve my knowledge and motivated me to always learn more, which I think will be very helpful in my future life.

I would like to thank my computational mentor Sinan Sevim (Susy Exists) for her guidance in our DFT and numerical studies. Susy started this project on NbSe₂ and CDWs way before me and when I joined she was already an expert in DFT. She thought everything I know about computations in the thesis and let me go over her own work whenever I needed. If she did not help me this much, my theses would not be here, at least in one piece.

I am would like thank for my research assistant colleagues at Istanbul Technical University for a great work environment and their friendship.

My family made everything so that I can keep my head down and type down this work. I am grateful for their support.

Finally, I am forever in debt to my beloved Duyguş, for keeping me sane and on track during this study. You make everything easier and joyful. I am so happy that you are in my life.

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ABBREVIATIONS

App	: Appendix
BZ	: Brillouin Zone
BOA	: Born-Oppenheimer Approximation
CDW	: Charge Density Wave
C-CDW	: Conventional Charge Density Wave
DFT	: Density-Functional Theory
EPC	: Electron-Phonon Coupling
EPW	: Electron-Phonon Wannier
FSN	: Fermi Surface Nesting
HF	: Hartree-Fock
HK	: Hohenberg-Kohn
NbSe₂	: Niobium di-selenide
PLD	: Periodic Lattice Distortion
PP	: Pseudo-Potentials
QE	: Quantum Espresso
TISE	: Time Independent Schrodinger Equation
TMDC	: Transition-metal di-chalcogenide
U-CDW	: Unconventional Charge Density Wave
W90	: Wannier90 Code



SYMBOLS

ω_q	: Softened phonon frequency
Ω_q	: Bare phonon frequency
χ_q	: Generalized static electronic charge susceptibility
χ'_q	: Static Lindhard charge susceptibility





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CHARGE DENSITY WAVES IN TRANSITION METAL DI-CHALCOGENIDES: A COMPARISON OF FERMİ SURFACE NESTING AND ELECTRON-PHONON COUPLING

SUMMARY

Charge density waves are ordered phases of matter in condensed matter physics. It is like a standing wave floating above the lattice which also has a phenomenon called periodic lattice distortion. A charge density wave and a periodic lattice distortion might come together on a material since electrical charges make the system come to a new ground state due to lattice-driven effects and the coupling between lattice and the electrons. A thought experiment made by Peierls paved the way going to the charge density waves. According to the Peierls, a 1-dimensional half filled band will go under a transition if the system is probed with a momentum of two times its wavevector. This is called Peierls instability. After several years, another scientist named Frölich wrote down a microscopic theory of electron-phonon coupling, which has the similar types of instability with the charge density waves.

According to Peierls, an instability paved the way for a mechanism called Fermi surface Nesting. It says that when there is a $\mathbf{q}$ vector connecting the opposite edges of the Fermi surface there will be an instability just like the as in the earlier idea of Peierls distortion/instability. This idea of Fermi surface nesting is feasible in 1-dimensional materials but as one uses higher dimensional materials Fermi surface nesting starts to fail. The reason for that, in two dimensional Fermi surfaces it is not easy to connect any point on the edges of the Fermi surface directly. The geometrical shapes of the Fermi surfaces are much more complex than their 1-dimensional counterparts. The amount of points that can manage to connect with CDW vectors is not enough to create an instability and hence, a CDW. A good measure of Fermi surface nesting in a material is a function called static Lindhard susceptibility. If there is a divergence in this function at some $\mathbf{q}$ point, that $\mathbf{q}$ point would be a good candidate for charge density wave instability.

At higher dimension, with Fermi surface nesting not working any more, new mechanisms are searched for since the first two dimensional observation of charge density waves in 1970s. To this day, there is still not any mechanism ideal for all cases or for all materials. Still, one has to run experiments or simulations for which mechanism is stronger in a specific material. The problem of determining fundamental mechanism between two candidates, which are Fermi surface nesting and electron-phonon coupling, will be the motivation of this study. We have a candidate material called NbSe₂, a member of the transition-metal di-chalcogenides family. After neutron and x-ray scattering experiments, we know that there is a $\mathbf{q}$ vector of charge density wave in the path Γ -M of the Brillouin zone. We run simulations to

observe the Lindhard susceptibility and electron-phonon coupling constant on this path. For these simulations we use DFT programs called Quantum Espresso and Electron-Phonon Wannier. After the calculations, we see that the electronic effects observed by searching for a peak value of Lindhard susceptibility, is not very effective or distinctive. Whereas, the electron-phonon coupling constant has a mighty peak just above the searched $\mathbf{q}$ vector. This gives the hint that for instabilities about that $\mathbf{q}$ point, electron-phonon coupling effects are much more effective, and materials NbSe₂ is identified as a $\mathbf{q}$ -dependent electron-phonon coupling material. For some researchers this corresponds to the type 2 CDW. The judgment of the which effect has more influence on the resultant instability is decided o their behavior on the $\vec{q}_{CDW} = 0.66(\Gamma - M)$. The peaks in graphs are quantitatively measured according to their elevation from the mean of their respective datasets. The peak of the electron-phonon coupling effect has showed %865 peak values, where the electronics effects which are probed with the Lindhard susceptibility has showed only %38 peak behavior.



GEÇİŞ METALLİ Dİ-KALKOJENLERDE YÜK YOĞUNLUK DALGALARI: FERMİ YÜZEYİ YUVALANMASI VE ELEKTRON-FONON ETKİLEŞİMİ'NİN KARŞILAŞTIRILMASI

ÖZET

Yoğun madde fiziğinde yük yoğunluk dalgaları, elektronik olarak düzene girmiş bir fazdır. Elektrik yüklerinden oluşan bir durağan dalga gibi düşünülebilir. Elektrik yüklerinin altında ise periyodik örgü kaymasına uğramış atomlar vardır. Yük yoğunluk dalgaları ve periyodik örgü kayması her zaman beraber gerçekleşen olaylardır. Bu fiziksel olayı ilk defa Rudolph Peierls'in öne sürdüğü kabul edilir. Peierls tam olarak şunu öne sürmüştür; yarım dolu 1-boyutlu bir elektronik bant eğer sistem elektronik bandın Fermi dalgavektörünün tam iki katı ile uyarlarsa bantlar üzerinde bir kararsızlık olacak. Peierls'ten daha sonra Frölich, mikroskopik bir süperiletkenlik teorisi öne sürmüş, bu teorinin yük yoğunluk dalgaları ile aynı kararsızlıklara sahip olduğunu fark edilmiştir. O zamandan beri süperiletkenlik ile yük yoğunluk dalgaları benzer mekanizmalara sahip fiziksel olaylar gibi düşünülüp aralarında bir ilişki kurulmaya çalışılmıştır. Günümüzde de hala popüler bir araştırma konusudur.

Yük yoğunluk dalgalarının oluşması teorik olarak 1 boyutlu malzemeler için geçerlidir. Bu fikri bir miktar ilerleterek 1 boyutta fermi yüzeyi yuvalanması olarak tanımlayacağımız bir olayı inceleyebiliriz. 1 boyutta bir malzemenin fermi yüzeyi birbirine bakan iki paralel levha gibi düşünülebilir. Bu iki levhayı birleştirmek, boyutu hiç değişmeyen bir $\mathbf{q}$ vektörü ile mümkündür. Fakat 1 boyuttan çıkıp iki boyuta yerleştiğimiz zaman, bu vektörün işi eskisi kadar kolay değildir. İki boyutta Fermi yüzeyini bir daire olarak alabiliriz. $\mathbf{q}$ vektörü eğer tam çap üzerinden dairenin iki tarafını birleştiriyorsa, çapın üzerinden başka bir yere koyduğumuzda hiçbir fermi yüzeyi parçasını birleştiremeyecektir. Bu neden Fermi yüzeyi yuvalanması, 2 ve daha yüksek boyutlu malzemelerde işlevsi hal gelmeye başlar.

Deneyisel olarak yük yoğunluk dalgalarının 2 ve daha yüksek boyutlu malzemelerde görülmesinden dolayı yük yoğunluk dalgalarını oluşturan başka fiziksel mekanizmaları araştırmak gündeme gelmiştir. Araştırmalara rağmen bugün hala yük yoğunluk dalgalarını sistemden bağımsız bir şekilde bir mekanizmayla açıklamak mümkün değildir. Genel kabul görmüş bir çalışma prensibine henüz sahip değildir. Farklı mekanizmalar ile oluşan yük yoğunluk dalgalarını açıklama çalışmalarında öne çıkan adaylardan biri fonon momentumuna bağlı elektron-fonon çiftlenmesidir. Yukarıda bahsedilen $\mathbf{q}$ vektörünün nerede olduğunu henüz teorik olarak kesinlikle bilmek mümkün değildir. Çünkü henüz tam anlamıyla güvenilecek bir teori yoktur. Bu nedenle nötron saçılmaları ile veya x-ışını saçılmaları kullanarak fonon diyagramları

incelenerek olası $\mathbf{q}$ vektörü noktaları bulunmaya çalışılır. Noktalar bulunduktan sonra, yük yoğunluğunu açıklamaya adaya mekanizmanın o $\mathbf{q}$ noktasındaki davranışı incelenir. Sistemde bir kararsızlık yaratacak mekanizmalar yük yoğunluk dalgalarını açıklamaya aday olabilirler.

Deney bir kere yapıp $\mathbf{q}$ noktası bulunduktan sonra, nümerik yöntemlerle aday mekanizmanın davranışı incelenebilir. Bu çalışma da tam olarak bununla ilgilidir. Geçiş metalli dikalkojenler ailesinden niobyumdiselenit (NbSe_2) malzemesinde yük yoğunluk dalgası fazı gözlenmektedir. Aynı malzemede daha düşük sıcaklıklarda süperiletken faz da gözlenmektedir. Bu nedenle NbSe_2 fazlasıyla araştırmacının ilgi duyduğu bir malzeme haline gelmiştir. Yük yoğunluk dalgası fazına sahip malzemelerin ayrıca taşınım özellikleri de değişmektedir. Bu nedenle teknolojik olarak ilgi duyulan ve mühendisliğe uygun özellikler taşımaktadırlar.

Malzememizi belirledikten sonra çalışma yöntemimiz olan yoğunluk fonksiyonel teorisine (YFT) geçebiliriz. YFT, son yıllarda hesaplamalı bilimlerin bilgisayar kapasiteleri ile son derece gelişmeleri ile önem kazanmıştır ve teorik, deneysel çalışmalara üçüncü bir alternatif olmaktadır. Bu çalışmada Quantum ESPRESSO (QE) ve Electron-Phonon Wannier (EPW) adlı kodlar kullanılmaktadır. QE ile malzemeyi bilgisayar ortamında gerçekleyip malzeme üzerindeki fonon frekanslarını, yük yoğunluğunun dağılımını, dalga fonksiyonlarını ve daha birçok özelliği hesaplayabiliriz. QE kodunu kullanabilmek için önce malzemenin atomik parametrelerini bilmek zorundayız. Bundan sonra YFT ile en düşük enerji ve taban durumları bulma altprogramlarını kullanarak. QE ile malzemeler gerçekleştirildikten sonra sıcaklık parametresini değiştirerek malzemenin düşük sıcaklıklardaki davranışını inceleyebiliriz. Frölich hamiltonyeninin çözümlerine göre eğer sistemde fermi dalgavektörünün 2 katı boyunda olan bir $\mathbf{q}$ vektörü noktası var ise düşük sıcaklıklarda fonon bantlarından birisi bir değişime uğrayarak frekansını sıfır değerine götürmeye çalışır. Bu olaya Kohn anomalisi denir. $\mathbf{q}$ vektörünün yerini kontrol etmek için önemli bir yöntemdir. Bu çalışmada çizdiğimiz fonon grafiklerinde Kohn anomalisi $\mathbf{q}$ vektörüne yakınsayan bir noktada gözlenmiştir EPW kodu ile de malzeme üzerinde Wannier fonksiyonlarını hesaplayarak aralarındaki interpolasyon işlemleri ile özenerji, elektron-fonon çiftlenme gücü ve sabiti gibi özellikler hesaplayabiliriz.

Amacımız NbSe_2 malzemesi için fermi yüzeyi yuvalanması ve elektron-fonon çiftlenmesi parametrelerini hesaplayıp daha önce deneysel olarak belirlenmiş yük yoğunluk dalgası $\mathbf{q}$ vektöründe bir tepe değeri yapıp yapmadıklarını kontrol etmektir. Eğer fermi yüzeyi yuvalanmasının etkisini kontrol etmek istersek, saf elektronik bir etki olan statik Lindhard duyarlılığını hesaplayabiliriz. Bu parametreyi EPW değerlerinin çıktısıyla hesapladığımızda NbSe_2 'nin belirlediğimiz ve yük yoğunluk dalgası $\mathbf{q}$ vektörünü barındırdığını bildiğimiz bir patikası üzerinde kayda değer bir tepe değeri görmemiş olduk. Bu demektir ki elektronik bir etki olan fermi yüzeyi yuvalanması bu malzeme üzerinden etkili değildir.

Yük yoğunluk dalgasını $\mathbf{q}$ vektörünü barındıran aynı patika üzerinde elektron-fonon çiftlenmesi sabitini hesaplarsak etrafındaki değerlerden ayrılan çok yüksek bir tepelenme görüyoruz. Bu bize $\mathbf{q}$ momentumuna bağlı elektron-fonon çiftlenmesi parametresinin bu malzeme için kararsızlık yaratabilecek kadar güçlü olduğunu gösteriyor. Doğrudan bir fonon etkisi olan fonon öz enerjisini hesaplayıp çizdirdiğimiz zaman yine aynı yük yoğunluğu dalgası $\mathbf{q}$ vektöründe bir tepelenme yaptığını görmüş oluyoruz. Bu bulgularla NbSe_2 malzemesinde etkili olan yük

yoğunluęu mekanizmasının elektron-fonon çiftlenmesi paramterlerine daha fazla baęımlı olduęunu kesinlikle söyleyebiliriz. Fermi yüzeyi yuvalanması mikroskopik olarak gerçekleşiyor olabilir. Fakat bir kararsızlık yaratacak kadar güçlü bir etkisi gözlenmemiştir.





1. INTRODUCTION

A charge density-wave is a ordered electronic phase in condensed matter physics. It can be thought as a standing wave of charge density. Oscillating above a distorted lattice. A CDW and a periodic lattice distortion always comes together because one of this events eventually cause to the other one. It was first proposed by Peierls [18]. What exactly Peierls proposed was that in a 1-dimensional half-filled electronic band, if the system is probed with a wave vector twice it's Fermi wave vector $q = 2k_F$, there should be an instability. Later, Frölich [19] proposed a microscopic superconducting theory which turns out to have similar instabilities with CDW formation. First observation of a experimental CDW is done by Fogle and Perlstein [20]. Since those days CDWs are heavily studied but a general "textbook" theory is still not constructed.

The mechanisms to explain the CDW formation is many-fold. In 1-dimensional systems, Fermi surface nesting stands out. Honoring the idea of Peierls, FSN says that if there is a vector that exactly connects the boundaries of Fermi surface of this 1D material, there will be a instability due to this connection. It will cause a divergence in the 1-dimensional Lindhard susceptibility. It is also possible to write down a weakly coupling mean field theory for the CDW dynamics which can explain the CDW gap formation after the instability. But it fails to carry on this success in higher dimensions than one [21].

In 2D FSN mechanism does not always hold. There are systems that their CDW formation can be explained with FSN but whether there is a certain mechanism underlying or not and this explanation is due to the suitable geometry of the Fermi surface is still under debate and results are not going well for the favor of FSN. Since the mechanisms are still unknown there are numerous candidates and research about 2D CDW formation. Some are; partial nesting vectors [22], excitons [23], electron-phonon coupling [24], exciton-phonon interaction [25] or metal-insulator transition [26]

In this work, electron-phonon coupling will be examined as a rival to the FSN. The material that will be examined will be the transition-metal di-chalcogenide 1H-NbSe₂. TMDC family of materials took the attention of the researchers. For certain temperatures some of them can be in superconducting phase or CDW phase. Since these two concepts can be examined together, TMDCs are also good candidates for superconductivity research. The material is also used for searching for a connection between CDW mechanisms and Superconductivity mechanisms [27]. One another reason for the study of CDW is the transport properties of the system change when

The analysis in this work will be a computational one. We will calculate the known signatures of FSN and EPC and try to decide which one is more effective. For this DFT analysis, Quantum Espresso and Electron-Phonon Wannier codes will be used.

The structure of this document is as follows; In chapter 2 necessary many-body physics terms are introduced. Also in this chapter conventional theoretical model of charge-density wave and the observation unconventional charge density waves are introduced. In chapter 3, the studied material NbSe₂ and its family of materials TMDCs are introduced. In chapter 4 the analysis method of density-functional theory is introduced and used programs are given. Steps for acquiring the simulation results are listed in terms of DFT steps. At the end of this chapter calculation results are given. In chapter 5, analysis of acquired data is made and this chapter concludes this study. In Appendix A, used input files for the programs are given.

2. MANY-BODY PHYSICS & CHARGE-DENSITY WAVES

2.1 Electrons, Phonons & Electron-Phonon Coupling

In second quantized form, electrons of a one dimensional free electron gas (under no potential) can be described using an hamiltonian in form;

$$H_{el} = \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}, \sigma} c_{\mathbf{k}, \sigma}^{\dagger} c_{\mathbf{k}, \sigma} \quad (2.1)$$

where $c_{\mathbf{k}, \sigma}^{\dagger}$ means a creation operator that will create an electron of momentum $\mathbf{k}$. For the phonons we can start from the Hamiltonian for lattice vibrations which is basically sum of kinetic and potential energy terms but with conjugate momenta and position;

$$H_{ph} = \sum_{\mathbf{q}, \lambda} \left[\frac{P_{\mathbf{q}, \lambda} P_{-\mathbf{q}, \lambda}}{2M} + \frac{M \omega_{\mathbf{q}, \lambda}^2}{2} Q_{\mathbf{q}, \lambda} Q_{-\mathbf{q}, \lambda} \right] \quad (2.2)$$

where $\omega_{\mathbf{q}, \lambda}$ is the frequency of phonon mode $\mathbf{q}$ and M is the atomic mass. Using the expressions

$$Q_{\mathbf{q}, \lambda} = \left(\frac{\hbar}{2M\omega_{\mathbf{q}, \lambda}} \right)^{1/2} (a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda}^{\dagger}) \quad , \quad P_{\mathbf{q}, \lambda} = \left(\frac{\hbar M \omega_{\mathbf{q}, \lambda}}{2} \right)^{1/2} (a_{\mathbf{q}, \lambda}^{\dagger} - a_{-\mathbf{q}, \lambda}) \quad (2.3)$$

the phonon Hamiltonian is found as [4, 28];

$$H_{ph} = \sum_{\mathbf{q}, \lambda} \frac{\hbar \omega_{\mathbf{q}, \lambda}}{2} (a_{\mathbf{q}, \lambda}^{\dagger} a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda} a_{-\mathbf{q}, \lambda}^{\dagger}) \quad (2.4)$$

where $a_{\mathbf{q}, \lambda}^{\dagger}$ is the creation operator for phonon mode $\mathbf{q}$ and $a_{\mathbf{q}, \lambda}$ is the annihilation operator for phonon mode $\mathbf{q}$. Adding the electron phonon momentum Hamiltonian;

$$H_{el-ph} = \sum_{\mathbf{q}, \lambda} (a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda}^{\dagger}) \Gamma_{\lambda}(\mathbf{q}) = \sum_{\mathbf{q}, \lambda} A_{\mathbf{q}, \lambda} \Gamma_{\lambda}(\mathbf{q}) \quad (2.5)$$

where

$$\Gamma_\lambda(\mathbf{q}) = \sum_{\mathbf{k}, \sigma} g_{\lambda, \sigma}(\mathbf{k}, \mathbf{k} + \mathbf{q}) C_{\mathbf{k} + \mathbf{q}, \sigma}^\dagger C_{\mathbf{k}, \sigma} \quad (2.6)$$

we arrive at the famous Fröhlich Hamiltonian $H = H_{\text{el}} + H_{\text{ph}} + H_{\text{e-ph}}$ [4, 29, 30];

$$H = \sum_{\mathbf{k}} \xi_{\mathbf{k}, \sigma} c_{\mathbf{k}, \sigma}^\dagger c_{\mathbf{k}, \sigma} + \sum_{\mathbf{q}, \lambda} \frac{\hbar \omega_{\mathbf{q}, \lambda}}{2} \left(a_{\mathbf{q}, \lambda}^\dagger a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda} a_{-\mathbf{q}, \lambda}^\dagger \right) + \sum_{\mathbf{q}, \lambda} \left(a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda}^\dagger \right) \Gamma_\lambda(\mathbf{q}) \quad (2.7)$$

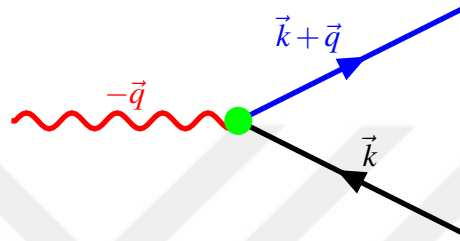


Figure 2.1 : Feynman diagram of the lowest-order process involving the electron-phonon interaction, the scattering of a single electron state with momentum $\mathbf{k}$ to a state with momentum $\mathbf{k} + \mathbf{q}$ by a simultaneous creation or annihilation of a single phonon of momentum $\mathbf{q}$ [1].

2.2 Conventional Charge Density Waves

The first exemplary model for a "charge-density wave" is proposed by Peierls [18], though it was not yet had this name it was rather a toy model to show an instability of an electronic system. Peierls instability is a phenomenon in condensed matter physics that occurs in one-dimensional (1D) systems. When the lattice is taken to elongate slightly, it will create a potential change accompanied with this shift of position. This distortion creates a periodic modulation in the charge density, resulting in the formation of a Charge Density Wave (CDW). This formation has to be energetically favorable (it should lower the overall system energy) to be maintained by the lattice structure. This is where the instability comes in. Just in the moment the conditions for a CDW formation is favorable energetically system undergoes a phase change The Peierls transition is a type of electronic phase transition associated with this instability. A 1-dimensional expression for CDW can be written as [29];

$$\rho(\mathbf{r}) = \rho_0 \left[1 + \rho_1 \cos(\mathbf{q}_{CDW} \mathbf{r} + \phi) \right] \quad (2.8)$$

where ρ_0 is the unperturbed electron density, ρ_1 , $\mathbf{q}_{CDW}$ and ϕ are the amplitude, wavevector and phase of the electron density modulation, respectively. The last term of equation 2.8 in the square bracket is called the CDW term.

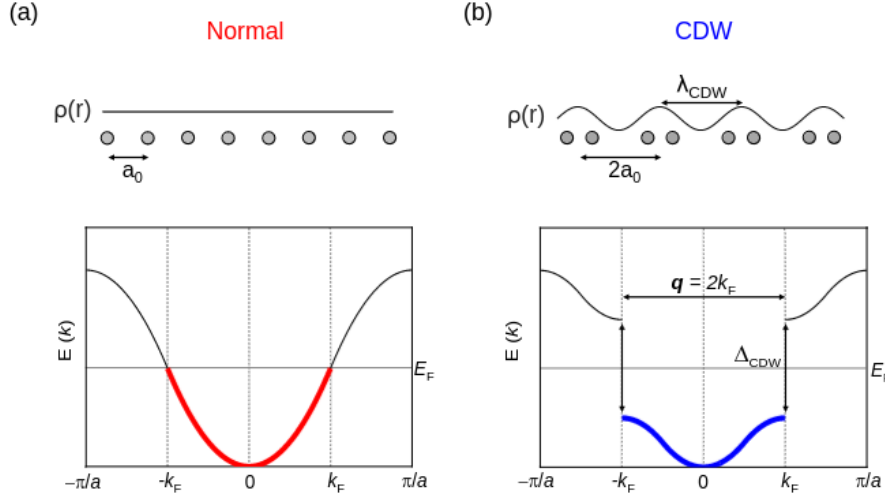


Figure 2.2 : 1D CDW Formation. (a) Normal electronic band dispersion. The atomic spacing is in regular form and equal to a_0 (b) After Peierls transition, CDW is formed on the charge distribution and lattice is moved to have a spacing of $2a_0$ under periodic lattice distortion. Here, λ_{CDW} stands for the $\mathbf{q}_{CDW}$ in Eq. 2.8 [2].

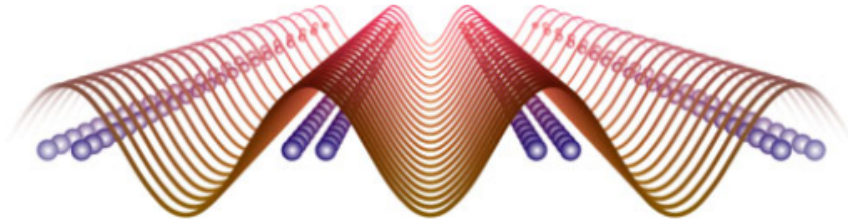


Figure 2.3 : Graphical representation of charge-density wave. Brown-red curves show the modulated charge densities and spheres indicate the ions on several lattice sites. [3].

This type of 1-dimensional, Peierls instability triggered CDWs are called conventional. Their mechanism is long known for decades. The energy balance can be calculated as follows. When a phonon changes places (it shifts a distance $u_{\mathbf{q}}$, where $u_{\mathbf{q}}$ is the static displacement of phonon mode $\mathbf{q}$) inside its chain of atoms it creates a potential. Using the definition of $g_{\mathbf{q}}$ [29], we can write it as;

$$v_{\mathbf{q},\lambda} = g_{\mathbf{q},\lambda} u_{\mathbf{q},\lambda} \sqrt{\frac{2M\omega_{\mathbf{q},\lambda}}{\hbar}} \quad (2.9)$$

Since the atoms moved inside a chain it will accumulate a energy in a similar fashion to Hooke's law;

$$\delta E_{\text{lattice}} = \frac{1}{2} M \omega_{\mathbf{q},\lambda}^2 u_{\mathbf{q},\lambda} \quad (2.10)$$

Since the potential is altered by the moving atom, electronic structure will feel that change as a perturbation, the change in the energy under the potential $v_{\mathbf{q}}$ is given as; [28, 29];

$$\delta E_{\text{e-band}} = -|v_{\mathbf{q}}|^2 \chi'_{\mathbf{q}} \quad (2.11)$$

where $\chi'_{\mathbf{q}}$ is defined as;

$$\chi'_{\mathbf{q}} = \frac{1}{L} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q},\sigma} - f_{\mathbf{k},\sigma}}{\epsilon_{\mathbf{k},\sigma} - \epsilon_{\mathbf{k}+\mathbf{q},\sigma}} > 0. \quad (2.12)$$

and called non-interacting electronic susceptibility. Here, L is the length of the atomic chain in discussion. The changes in the energy must be sum up to some negative number, $\delta E_{\text{lattice}} + \delta E_{\text{e-band}} < 0$, and this gives a condition of;

$$\frac{4g_{\mathbf{q},\lambda}^2}{\hbar\omega_{\mathbf{q},\lambda}} > \frac{1}{\chi'_{\mathbf{q}}} \quad (2.13)$$

as long as the condition 2.13 is satisfied system will undergo a CDW phase transition. When the condition is satisfied, energy loss of the energy gap reduction is greater than the elastic energy of lattice distortion whole system will in favor of phase transition, this will also result in a conductor to insulator transition [31]. Susceptibility function 2.14 plays an important role in finding the CDW transition points in q-space. In figure 2.18 one can see that in 1-dimension there is a sharp peak on top of nesting vector $\mathbf{q} = 2k_F$. Checking the definition of the non-interacting electronic susceptibility, we can expect that divergence since the denominator will give exponentially large numbers as $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}+\mathbf{q}}$ numerically catch up. If the $\mathbf{q}$ vector connects two spots on the Fermi

surface then we have $|\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}| \approx 0$ then we have a divergence, or depending on the success of the nesting vector $\mathbf{q}$, a very high divergence value.

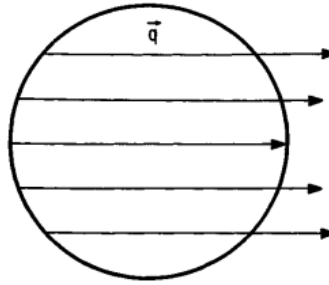
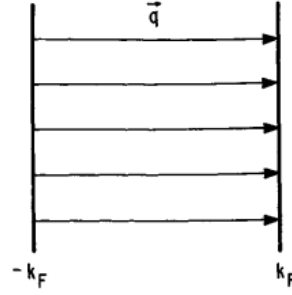


Figure 2.4 : Different shapes of free electron gas Fermi surfaces. The upper one belongs to a 1-dimensional system where the lower is a 2-dimensional system. It can be seen that a constant length vector $\mathbf{q}$ in a circular geometry is not as successful as connecting the points on Fermi surface as it was in a 1D case on top. [4].

2.3 Unconventional Charge Density Waves

While that was the situation in 1-dimension, when the dimensions of the material increases, as it can be seen, from the figure 2.5, the divergent behavior starts to fade away. One approximate theory except nesting of the Fermi surface for the quasi-1D systems is the weak coupling mean field theory. It may give appropriate results for the conventional CDW systems but it does not for systems of dimensions of two and higher [21]. In 2D and higher-dimensional materials, the analysis used for conventional charge density waves is insufficient and new underlying mechanisms are searched for years.

As the temperature of the monolayer transition metal-dichalcogenide system decreases and the relaxation calculations of atoms are made below some critical temperature specific to the material CDW appears. With this CDW formation the real space atomic

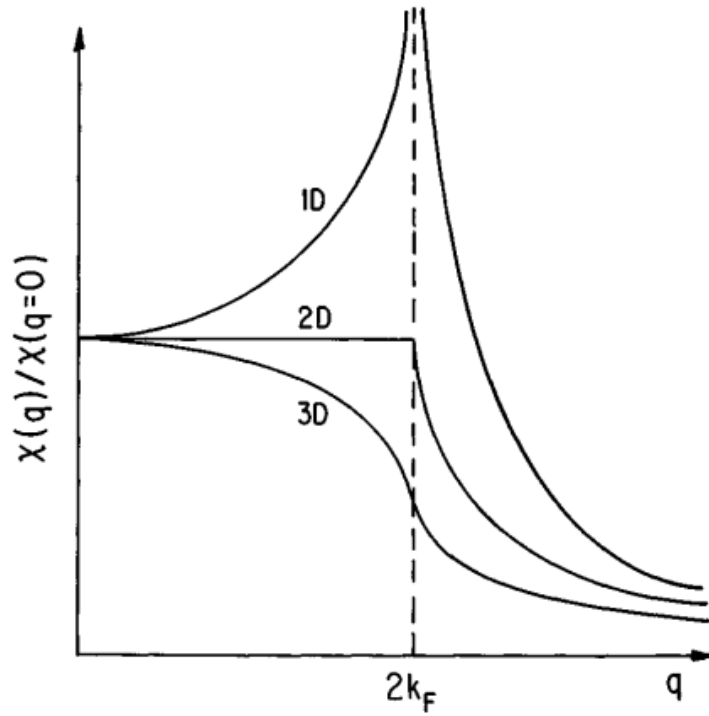


Figure 2.5 : Phonon wavevector dependent Lindhard response function for 1, 2 and 3 dimensional free electron gas at $T = 0$ K [4].

positions and cell parameters suffers a periodic lattice distortion. The results and connection between the two can be seen in Fig. 2.9. PLDs happen due to lattice dynamics and electron-lattice couplings

The insufficiency of the nesting mechanism can be understood deeper by analyzing Fig 2.4. On the upper side of the figure one can see a 1-dimensional system and hence it's Fermi surface. In 1D the Fermi surface resembles the shape of a parallel-plate capacitor. Given a constant magnitude $\mathbf{q}$, this $\mathbf{q}$ can connect infinitely many points on both side of the Fermi surface (it connects energy states of $-k_F$ and k_F). If we remember the denominator of Eq. 2.12, the amount of energetically close connected states contributes to this susceptibility function. We can see here that geometrical factors directly affects the susceptibility behavior. Now if we look on the second circular geometry in Fig. 2.4 ,which is a Fermi surface of a 2-dimensional electron gas system, a constant $\mathbf{q}$ cannot connect as many points as it did in 1D geometry. Again thinking the denominator of the susceptibility function in 2.12 the candidate $\mathbf{q}$ cannot create the singularity in the susceptibility and hence, there is a decrease in the effectiveness of the nesting mechanism. This crucial effect of system dimensions and FS geometry is also seen in Fig. 2.5. As it can seen in the figure, for 1D system there

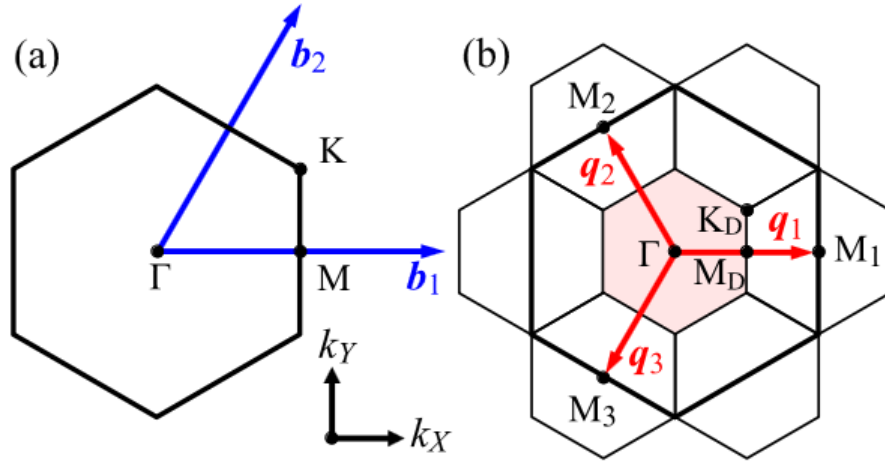


Figure 2.6 : (a) Reciprocal space vectors of the material 1T-TiSe₂ (b) An example picture of how multiple (triple in this case) $\vec{q}$ vectors would look like in BZ [5].

is a meaningful singularity (or asymptotic behavior), in 2D there is constant behavior and a following decrease without and peaks, finally in 3D, due to one more dimension and the complexity of Fermi surface that comes with it, there is no abnormal behavior in the susceptibility function χ_q .

According to the dimensionality of the system, there should be different types of CDWs; if the system is under the governance of FSN then it can be called type 1, if it is mostly affected by EPC it can be type 2 lastly if it's mechanism is charge modulation it is called type 3. Type 3 materials are mostly cuprates [32]. So we will not delve into type 3 since TMDCs are our materials. For the rest of this work. Mechanisms of type 1 and type 2 will be compared. As the dimensions increases, it is harder for a nesting vector to connect two sides of a Fermi surface. So at higher dimensions FSN fails as a CDW driving mechanism. Thinking from another way in terms of energies As the number of dimensions is increased, divergence at $|\mathbf{q}| = 2k_F$ is gone since in the denominator, number of states that are close in terms of energy are decreased which makes the divergence to converge at some value.

Other possible candidate mechanisms for the CDW formation is diverse. But there is no single winner for the whole periodic table. Exemplary mechanisms are partial nesting vectors [22], Jahn-Teller distortion or electron-hole correlations [2].

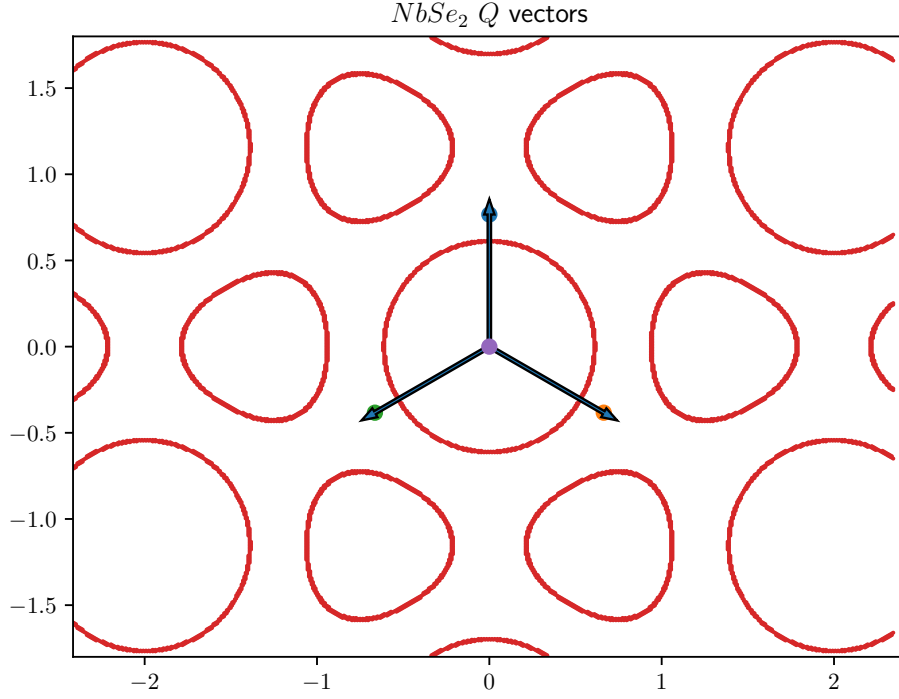


Figure 2.7 : Candidate nesting $\mathbf{q}$ vectors for 1H-NbSe₂. The red rounded shapes shows the Fermi surface edges of the material NbSe₂. Vectors $\mathbf{q}$ here will be used to connect any two points on these Fermi surface contours. The higher amount of connections between the contours by the $\mathbf{q}$ will positively contribute to the electronic susceptibility mechanism in the material.

2.3.1 Fermi Surface Nesting

Fermi surface nesting is a phenomenon that boundaries of multiple Fermi surfaces sits on top of each other when translated by a special $\mathbf{q}$ vector. The $\mathbf{q}$ vector that enables this event is called *nesting vector*. This mechanism is believed to be a triggering candidate for Peierls mechanism [31].

When the mechanism of the CDW is explained in terms of Fermi Surface Nesting (FSN), the arguments are very similar to the ones of Peierls transition (instability) in one dimension. But as the number of dimensions increase it gets harder for nesting vectors to connect the edges and boundaries of the Fermi Surfaces of the material [2]. It depends on the FS of the material. Even in high dimensions the material can accommodate more proper, parallel shapes of Fermi surfaces but it then depends on the character of the FS of the materials and cannot arise as a microscopic theory of CDW.

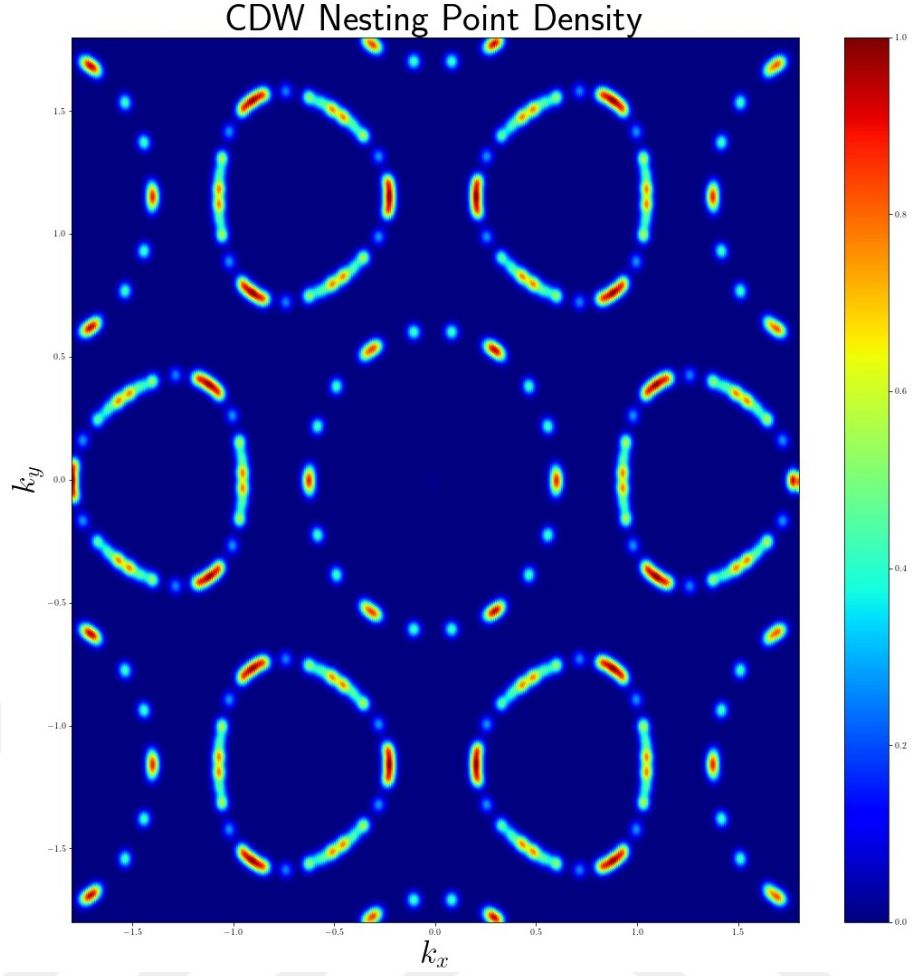


Figure 2.8 : Nesting point density in monolayer 1H-NbSe₂. Hot points (higher values in the right colorbar) indicates where the density of the points that can be connected with the nesting vectors $\mathbf{q}$ of the material [6].

Unsuitability of higher dimensions can be discussed further with multiple $\mathbf{q}$ vectors. A set of $\mathbf{q}$ vectors inside its respective Brillouin zone for another material TiSe₂ is given in Fig. 2.6 As we have seen with the circular Fermi surface geometry above, as the geometry of the Fermi surface gets more complex it is harder for the multiple $\mathbf{q}$ vectors to connect neighboring Fermi surface pieces gets harder. The situation for our material 1H-NbSe₂ is given in Fig. 2.7. Here, the red lines designate the Fermi surface and three vectors in the middle are our nesting vectors. One has to see if there is enough points connected by these three vectors on the red lines. The following calculation In Fig. 2.8 aims to answer this question. In this figure there is a summation going over all of the Fermi surface points, meanwhile comparing the 2-dimensional distance between every Fermi surface point couple in the system. In this search if there is a match between the 2D distance and the $\mathbf{q}$ vectors' length that combination will be stored as a nesting point. After that, we have the list of x and y coordinates of available nesting points.

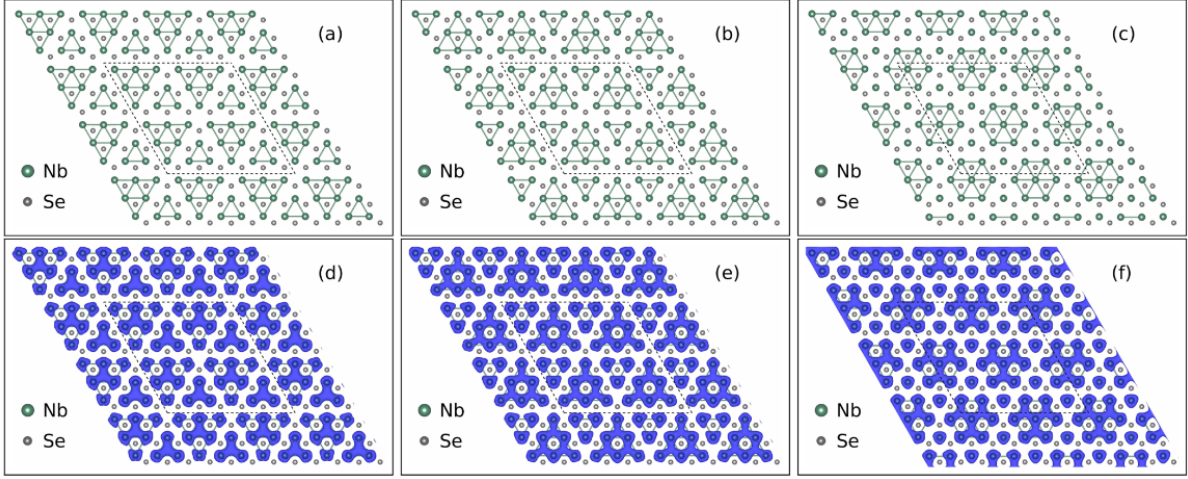


Figure 2.9 : Relaxed 1H-NbSe₂ structures with different geometric configurations. First row pictures (a),(b),(c) are the real spaces relaxed structures. In the lower row (d),(e),(f) are their respective charge densities [7]

To acquire the color map a Gaussian function is used. To every available nesting point in the system a Gaussian function is placed. Since there is a spread for every Gaussian function if the nesting points come close to each other (which means there are a lot of them in a small section) these Gaussian functions will add up and create the heat map. There are successful points to reach nesting condition in the system as designated by the red hot points in the figure. But the scarcity of these points in the overall scheme of the Fermi surface is not enough to say that FSN has a dominant effect in this material. This notion is supported by the calculated susceptibility function for the material NbSe₂ in Fig. 4.12.

To determine if FSN is a capable mechanism for CDW, we will use the static Lindhard susceptibility again and look for peaks in the χ function. I will cite the equation again, this time without the linear chain L parameter we have used above.

$$\chi'_q = \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q},\sigma} - f_{\mathbf{k},\sigma}}{\epsilon_{\mathbf{k},\sigma} - \epsilon_{\mathbf{k}+\mathbf{q},\sigma}}. \quad (2.14)$$

2.3.2 Electron-Phonon Coupling

For the 2D materials, CDW formation mechanism of FSN is not enough to trigger a lattice distortion, so the electron-phonon coupling has an effect on CDWs [31]. The hint where EPC might be effective might be given by using a phenomenon called Kohn

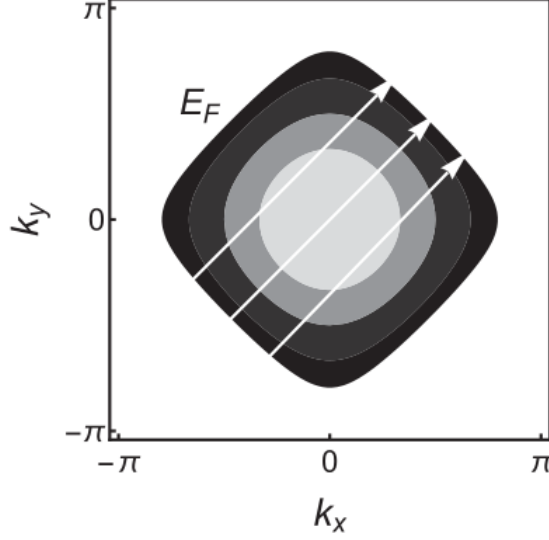


Figure 2.10 : Example figure for Fermi surface nesting. White vectors connects the edges of the fermi surface on the BZ of a 2D square lattice [8].

anomaly. The solution of the equation 2.7 is given by a formula which normalizes the phonon energy [32];

$$\omega_{\mathbf{q},\lambda}^2 = \Omega_{\mathbf{q},\lambda}^2 - 2\Omega_{\mathbf{q},\lambda}\chi_{\mathbf{q}} \quad (2.15)$$

where $\Omega_{\mathbf{q}}$ is the bare phonon frequency, $\omega_{\mathbf{q}}$ is the softened (normalized) frequency and $\chi_{\mathbf{q}}$ is given as $\bar{g}_{\mathbf{q}}\chi_{\mathbf{q}}$ and described below. For values of $\mathbf{q} = 2k_F$ value of the softened frequency goes down. This event is called *Kohn Anomaly* in phonon dispersion values. An example of the Kohn Anomaly in our simulations can be seen in figure 4.9.

The effect of electron-phonon coupling will be seen purely from the $\mathbf{q}$ -dependent electron-phonon coupling constant [9]:

$$\bar{g}_{\mathbf{q},\lambda} = \sum_{\mathbf{k}} |g_{\mathbf{k},\mathbf{k}+\mathbf{q},\lambda}|^2 \quad (2.16)$$

The coupling constant g is dependent on $\mathbf{q}$ since when the electronic wave function is a single plane wave we have the equation [33];

$$g_{\mathbf{k},\mathbf{k}'} = -i\epsilon(\mathbf{q}) \cdot (\mathbf{k}' - \mathbf{k}) \left[\frac{\hbar}{2MN\omega_{\mathbf{q},\lambda}} \right]^{1/2} V(\mathbf{k}' - \mathbf{k}). \quad (2.17)$$

Since the electron-phonon matrix elements for the phonon emission are zero unless the momentum condition is satisfied. The condition required is $\mathbf{k} = \mathbf{k}' + \mathbf{q} + \mathbf{G}$ where $\mathbf{G}$ is

the reciprocal lattice translation vector. If we put this condition to the eq. 2.17 above we can see that there is q dependence on the electron-phonon coupling constant. This approximation is valid when electrons can be considered as plane waves, assuming the electrons and lattice coupling is small.

The combination of $\bar{g}_q$ and Lindhard susceptibility χ'_q is the generalized static electronic susceptibility. χ_q is given as [9, 34];

$$\chi_q = \sum_{\mathbf{k}} |g_{\mathbf{k}, \mathbf{k}+\mathbf{q}, \lambda}|^2 \frac{f_{\mathbf{k}+\mathbf{q}, \sigma} - f_{\mathbf{k}, \sigma}}{\epsilon_{\mathbf{k}, \sigma} - \epsilon_{\mathbf{k}+\mathbf{q}, \sigma}} \quad (2.18)$$

where $f(\epsilon_{\mathbf{k}})$ or $f_{\mathbf{k}}$ is the Fermi-Dirac distribution function at energy $\epsilon_{\mathbf{k}}$ and $g_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ is the EPC matrix element that couples electronic states $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ with a phonon of momentum $\mathbf{q}$. This coupling process is also shown in the Feynman diagram in figure 2.1. Also to see the effect of EPC on $\mathbf{q}_{\text{CDW}}$ we will calculate the *phonon self energy*. Phonon self energy is given as [35];

$$\Pi_{\mathbf{q}\nu} = \sum_{mn, \mathbf{k}} w_{\mathbf{k}} \left| g_{mn, \nu}^{SE}(\mathbf{k}, \mathbf{q}) \right|^2 \frac{f(\epsilon_{n\mathbf{k}}) - f(\epsilon_{m\mathbf{k}+\mathbf{q}})}{\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega_{\mathbf{q}\nu} - i\eta} \quad (2.19)$$

A nice set of results from the literature is given in figure 2.11 down below. I will use these to verify my result at the conclusion part.

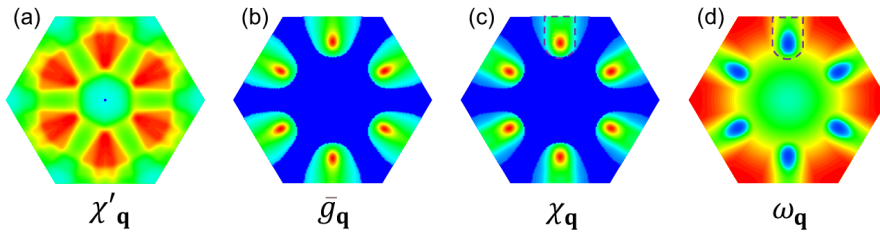


Figure 2.11 : Plotting generalized electronic susceptibility parameters onto Brillouin zones of 1H-NbSe₂ (a) Static Lindhard Susceptibility (b) $\mathbf{q}$ -dependent EPC (c) generalized static electronic susceptibility (d) lowest phonon branch frequency values. Adapted from [9]

3. MATERIALS

3.1 2D Materials

In the realms of physics and materials science, 2D materials have emerged as extraordinary experimental candidates, so in recent years they gain a lot of attention. Comprising single or few atomic layers, these materials, such as graphene and transition metal di-chalcogenides, exhibit remarkable and emergent electronic, optical, and mechanical characteristics. Being emergent is important because it leads researchers who are experimentalists and theorists work together to tackle the unknowns of these materials. Experiment and theory (and also ab-initio numerical calculations) benefit each other in this field since none of them can by themselves capture the emergent properties of these materials. The two-dimensional are promising candidates to have applications in electronics, optoelectronics, and beyond. As a recent and alluring field of scientific exploration in condensed matter physics field, 2D materials offer a fascinating playground for understanding fundamental quantum phenomena and pushing the boundaries of material engineering.

3.2 TMDCs

The chemical notation of TMDCs are given as MX_2 . Here, M stands for the transition metal of the compound and X stands for the chalcogen (oxygen family, since in the periodic table their column starts with the oxygen element) element. The unit cell structure stays same for all of these kind of materials. The metal atom is between two sheets of chalcogen atoms. TMDC materials are categorized according to their lattice structure. Main groups of structures are 1H and 1T, while the other structures being variations or stackings of these main ones. Representations of these different phases of 2D TMDCs are given in Figure 3.1. Difference between the 1H and 1T phases can be seen in Figure 3.2. While in the 1H systems consequent layers of the same element, let's say Se in our case, coincide and called as ABA structure; 1T systems

have consequent layers with a small shift with respect to each other and named ABC structure. The symmetry of the stacking is broken with respect the "B" layer of the structure in the ABC configuration, so we can say that ABC is less stable than ABA [10].

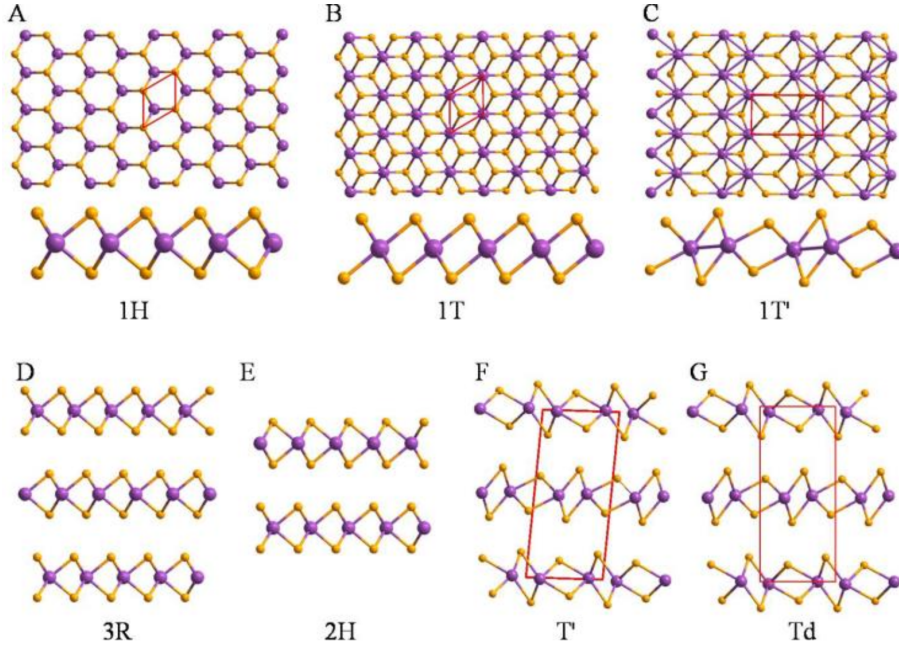


Figure 3.1 : Different phases of 2D TMDC lattice structures: (A) 1H, (B) 1T, (C) 1T', (D) 3R, (E) 2H, (F) T' and (G) Td phases [10].

3.3 NbSe₂

Niobium di-selenide (NbSe₂), is a member of the transition metal di-chalcogenide (TMDC) family, has drawn attention in recent years due to being host to some diverse physical phenomena. Hexagonal structure of the material is shown in figure 3.4 Exhibiting superconductivity at relatively high temperatures, NbSe₂ has become an important material for room temperature superconductivity research.. Its layered structure facilitates diverse electronic behaviors and intriguing charge density wave transitions. The breakthroughs in understanding NbSe₂'s electronic structure and its interaction with external stimuli have opened the way for applications in quantum devices and information processing. Researchers continue to explore the properties of NbSe₂, making it a compelling subject for both fundamental studies and technological advancements in condensed matter physics. In bulk NbSe₂ a CDW sets in at $T_{CDW} = 33$ K. Superconductivity sets in at $T_C = 7.2$ K. Below T_C these electronic states coexist but their microscopic formation mechanisms remain controversial. 3×3 CDW

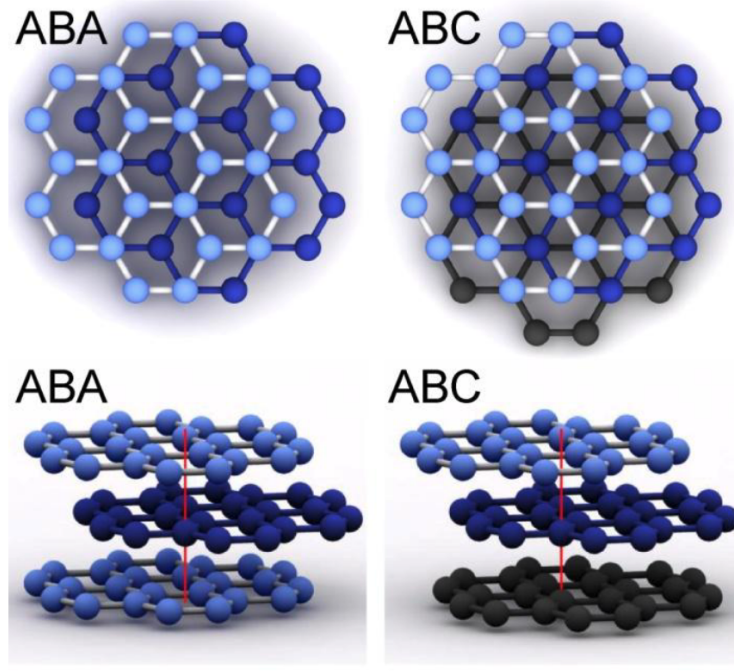


Figure 3.2 : ABA and ABC stacking of atomic layers. Where top and the bottom layer coincide in ABA, there is a shift between them in ABC [11].

order in NbSe_2 remains intact in two dimensions [36]. The surface images of the material NbSe_2 is given in figure 3.3. Our plots will be constantly drawn onto the path $\Gamma - \text{M} - \text{K} - \Gamma$. This path on the BZ of the material, is shown in 3.10

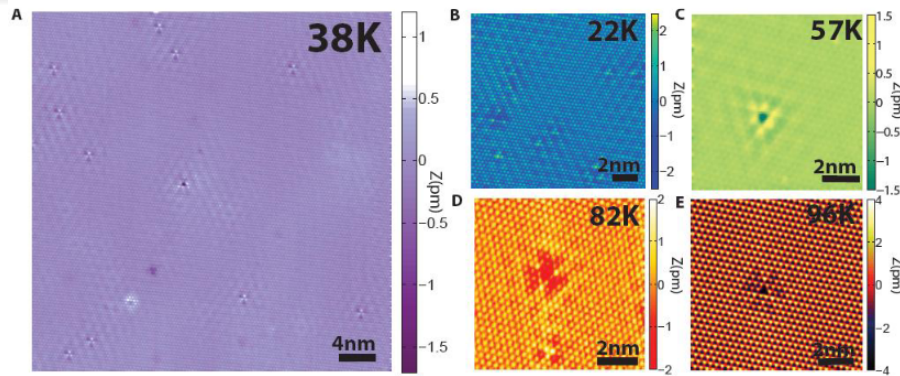


Figure 3.3 : STM image of the NbSe_2 surface for higher temperatures than T_{CDW} [12]

3.3.1 Modifications for Monolayer Calculations

Obtaining the monolayer 1H-NbSe_2 is pretty straightforward. We had two layers in the original structure given in figure 3.4. We choose one set of Nb atoms and delete it with it's neighboring Se atoms. Then we shift the remaining Nb atom to the center of the unit cell. The resulting structure is given in Figure 3.7.

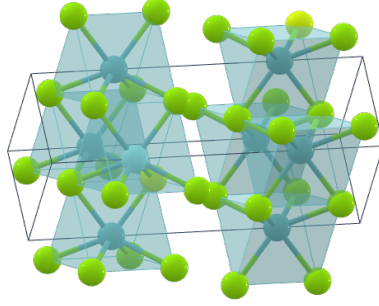


Figure 3.4 : 2H-NbSe₂ cell structure data file. Figure created with VESTA [13]

3.4 Experimental Results for $\vec{q}_{CDW}$

The studies to locate the $\vec{q}_{CDW}$ of the material 2H-NbSe₂ is done via neutron scattering experiments. The $\vec{q}_{CDW}$ vectors for the niobium di-selenide is found around $\frac{2}{3}\Gamma - M$ point [37]. This is an experimental result and we will assume that these are the real values since any model we can use does not have any confirmation for being microscopically true. The given results show a little spread in the location. If we add an error parameter δ , the spread is given as $\vec{q}_{CDW} = (1-\delta)\frac{2}{3}(\Gamma - M)$ with $\delta \approx 0.015-0.02$ [14,38]. In Fig. 3.5, The little bump of the NbSe₂ can be seen on the upper curve. The dip of the phonon branch is not low as in the Kohn Anomaly situation but this is due to the high temperature of the experimental environment. But we can see the clear behavior of dipping around two thirds of the way. There are also STM studies indicates the correct CDW peak with the δ spread of 0.143 [15,37].

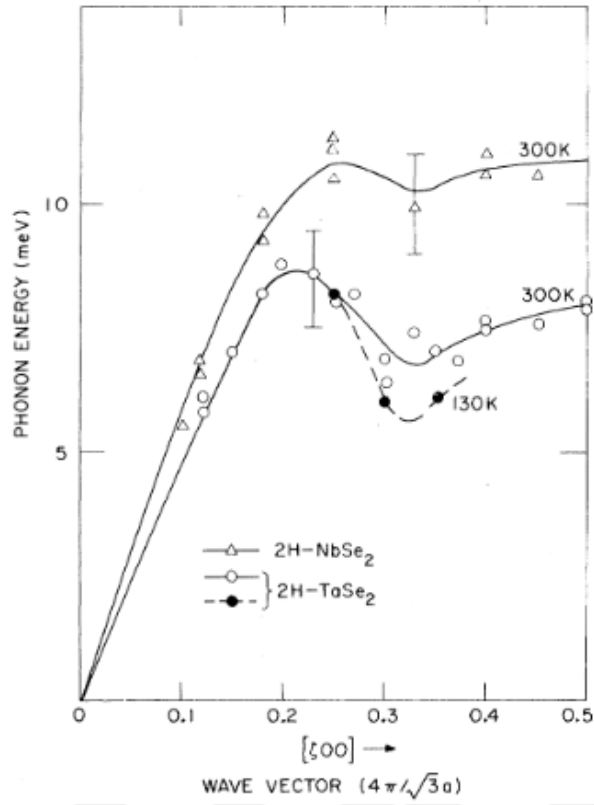


Figure 3.5 : Dispersion relations along $\Gamma - M$ line of the materials 2H-NbSe₂ and 2H-TaSe₂ [14]

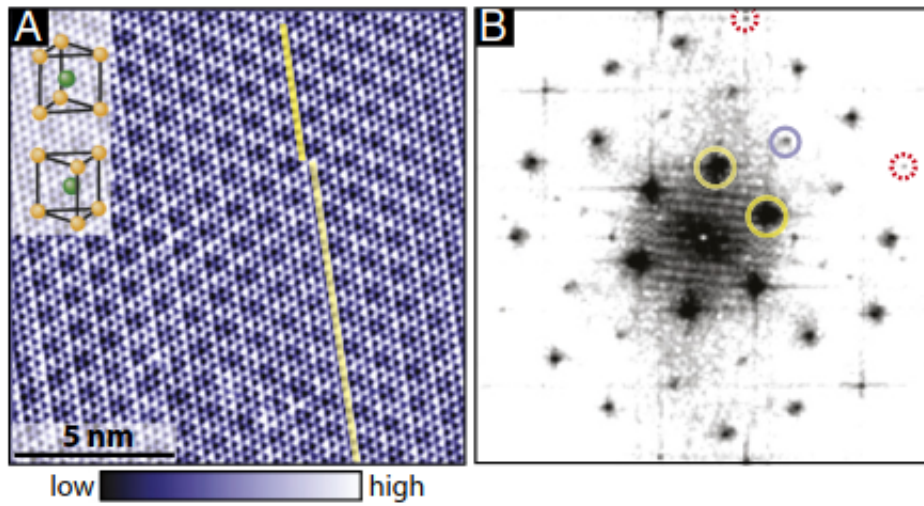


Figure 3.6 : STM images of a triple- $\vec{q}$ CDW. (A) Atomic resolution image showing 3x3 CDW. (B) Reciprocal space image of the CDW in A [15]

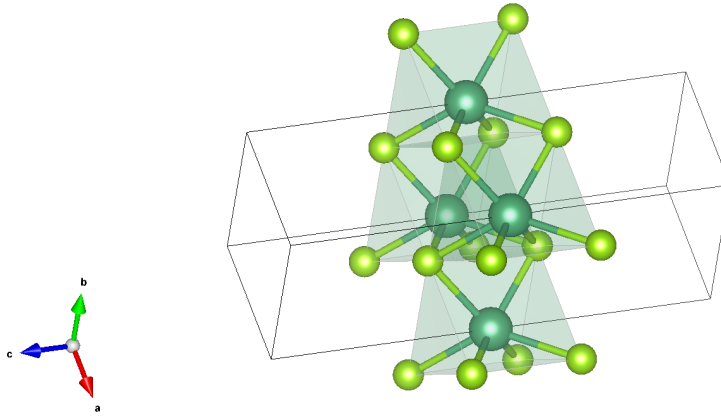


Figure 3.7 : Monolayer 1H-NbSe₂. The structure is modified so that one layer is omitted and the remaining layer is shifted to the middle of the cell in the z-axis (c-axis, or blue arrow, in the figure). Figure created with VESTA [13]

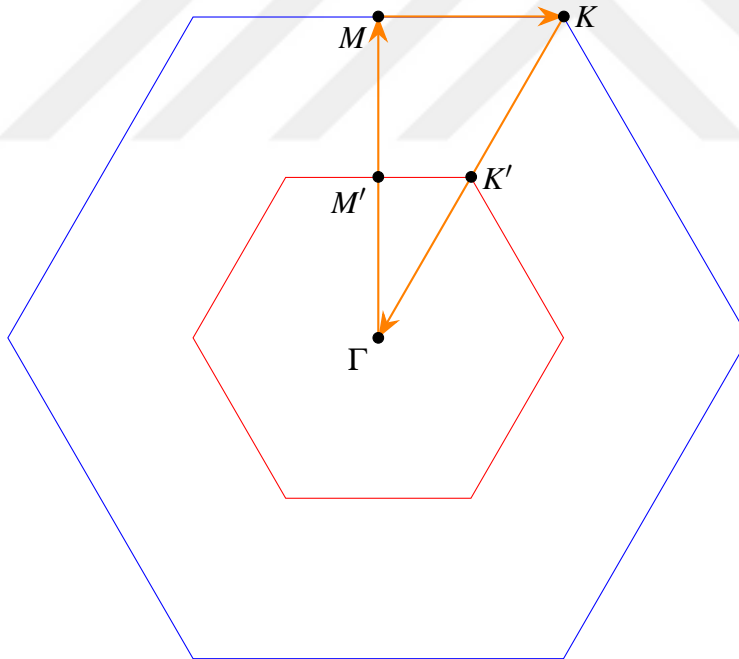


Figure 3.8 : BZ folding for a hypothetical supercell, the blue cell can be taken as the original BZ of the material for single cell, when a supercell is formed, the new lattice parameter in the real space enlarges by a factor of the multiplication of real cell, but its counterpart in reciprocal space shrinks by a factor of extension in real space. Red cell show the small reciprocal unit cell of the supercell.

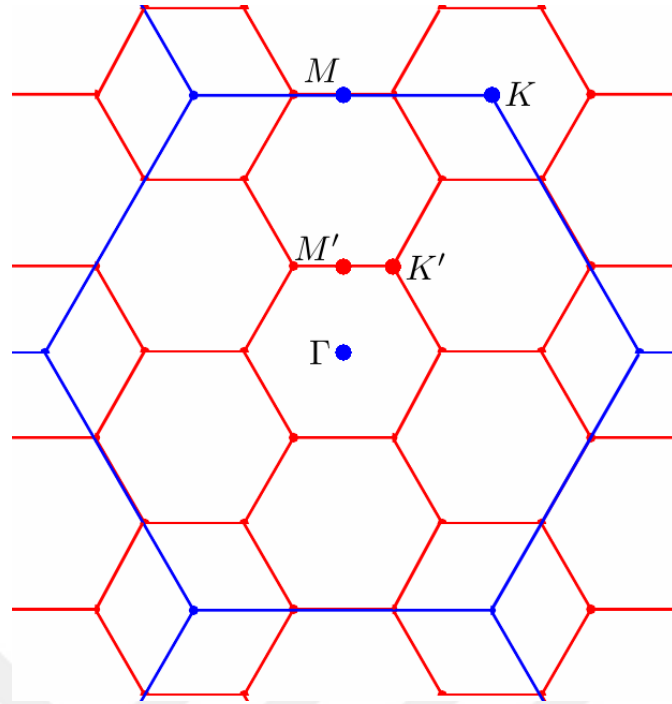


Figure 3.9 : BZ of original real space cell (blue), drawn with the same material's 3x3 real space cell's BZ (red).

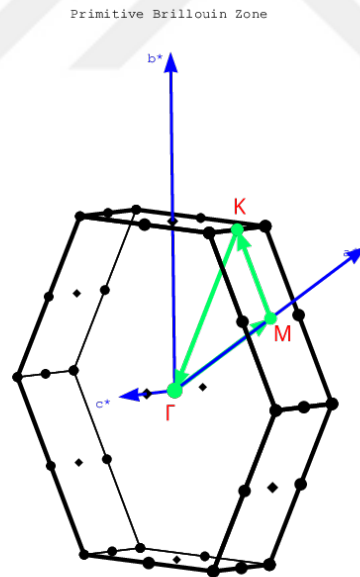


Figure 3.10 : Primitive Brillouin zone of monolayer 1H-NbSe₂. Blue vectors show the reciprocal unit vectors. Green path shows the k-path used the plot the graphs in this work. Green arrows follow the path $\Gamma - M - K - \Gamma$. Figure created by XCrysDen [16]



4. DENSITY FUNCTIONAL THEORY & AB-INITIO SOFTWARE

In this chapter a summary of theoretical background of DFT with its historcial progression will be given. Later on, approximations and pseudo-potentials will be introduced and finally, the software used during this work will be explained with emphasis on their individual computational steps.

In condensed matter physics all knowledge of a certain system at the level of atoms and electrons can be known if one solves the Schrodinger equation with the following most general Hamiltonian;

$$H_G = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_n \frac{\mathbf{P}_n^2}{2M_n} + \frac{1}{2} \sum_{ij, i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{nn', n \neq n'} \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} + \sum_{n,i} V_n(\mathbf{r}_i - \mathbf{R}_n) + H_{\text{other}} \quad (4.1)$$

where the first term on the r.h.s is the kinetic energy of loosely bounded itinerant (valence) electrons on the outer shells, second term is the kinetic energy of the atomic nuclei due to their relatively small motion compared to the valence electrons, third one is the Coulomb potential energy interaction between the electrons, fourth term is the Coulomb energy term of the nuclei of different atoms including their atomic numbers and the last term is the coupling of electrons to the bounding potential of atomic nuclei. The last term H_{other} is dependent on the model being examined. It can be an external electric field or a magnetic field. It can also be spin-orbit coupling or relativistic corrections [39].

The effort of calculating exact coordinates and energies at any time from this Hamiltonian is useless and not practical since the degrees of freedom for the system are at least at the order of 10^{23} . A simple calculation can be carried as follows; since this is a computational study let us have a personal computer with a processor clock speed of 3 GHz. This means it can make 3 billion calculations in one second. Assume that one calculation means finding the exact location $\mathbf{r}$, not even the velocity since it requires calculations using the positions, of a particle. There are approximately on the

order of 10^5 seconds in a day. So, for this computer to calculate only the positions of one mole gas, it would require 10^{17} days [40]. Even this crude calculation shows that exact solutions of atomic world is not feasible and practical. Approximations are a *must* in this field. Approximations are used to eliminate some of the degrees of freedom or some of the terms in equation 4.1. The feasible number of atoms to be used in calculations is around order of 10^2 even with the most powerful supercomputers. This number also varies with the type of the atom. Heavy atoms like Nb or U, make calculations more difficult and converging of the values takes more time. In the recent years, machine learning applications are heavily utilized in this field to reduce the number of simulations needed. The main goal here is to run simulations with some important parameters and fill the gap between these key parameters with interpolations obtained from ML models [41].

An important simplification of equation 4.1 is to write the Hamiltonian in an unit system called *Hartree atomic units*. These units are;

- 1 Hartree = 27.2114 eV
- 1 Bohr = 0.529 Å
- 1 atomic unit of mass = 9.1093×10^{-31} kg
- 1 electron charge is set to 1

Using Hartree system and plugging in quantum mechanical momentum operators we have a more simpler Hamiltonian of form [17];

$$H_{G,\text{Hartree}} = -\sum_i \frac{\nabla_i^2}{2} - \sum_n \frac{\nabla_n^2}{2M_n} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{n \neq n'} \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}_{n'}|} - \sum_{i,n} \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} \quad (4.2)$$

This form is more suitable for first-principle calculations since it only requires atomic number Z and atomic masses M .

As a first approximation we can use *Born-Oppenheimer Approximation* (BOA). BOA is an approximation regarding the atomic nuclei. Due to the enormous mass difference of electrons and nuclei ($M/m \approx 10^3 - 10^4$) nuclei will not instantaneously depend

on sudden changes of electron configuration due to their inertia stemming from the mass difference. So we can take the nuclei as stable particles in an electron sea. This removes the second term on the r.h.s of equation 4.1. Notice that the charge of the nuclei is still there, and electron-nucleus electrostatic interaction term is still present. This approximation also makes the nuclei-nuclei interaction constant. Since the nucleus charge is still there, but they are assumed not moving this first assumption of BOA is called clamped-nuclei approximation. So we can take it to the energy side in time independent Schrodinger equation. This enables us to write the equation 4.2 only in terms of electronic positions $\mathbf{r}_i$;

$$H_{G,\text{ele}} = -\sum_i \frac{\nabla_i^2}{2} + \sum_i V_n(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4.3)$$

where,

$$V_n(\mathbf{r}) = -\sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \quad (4.4)$$

Born-Oppenheimer Approximation is sometimes called as *adiabatic approximation*. First we can explain how adiabatic approximation works and figure out their relation later. Adiabatic approximation is basically a term used to describe the changes that happen under the equilibrium conditions. For our case, it stands for the equilibrium conditions of electrons. Since the electrons are attached to the nuclei under a electrostatic force any change in the atoms motion heavily affect the electrons' motion. The opposite is not true because the mass difference between the nuclei and electrons make nuclei nearly "immovable" under electronic movement. If the motion of the nuclei, is done under slow and small steps while allowing electrons to re-adjust themselves in their equilibrium conditions at every instant of the motion, we call this movement adiabatic. Adiabatic movement indicates there is relatively small electron-phonon coupling constant since phonon coupling is small enough to let electrons go back to their equilibrium positions. In other words as stated in [34], under the adiabatic approximation the atomic cores can be taken as fixed in position during electron dynamics time scales. The relation between BOA and adiabatic approximation is more clear, in BOA the nuclei is kept fixed in position to get rid of the kinetic energy term of the nuclei in the full Hamiltonian, whereas in adiabatic approximation

nuclei movement is so slow that the electrons "think" they are not moving or they have time to tolerate that movement. Combining two approximations in this paragraph Born-Oppenheimer approximation can be thought as clamped nuclei approximation and adiabatic approximation.

When the time scales and movement does not allow electrons to relax their coordinates every step of movement, we are in the non-adiabatic region. Non-adiabaticity means that phonons (nuclei movement) and electrons are strongly correlated and change of position one cannot be neglected by the other. In DFT scheme non-adiabatic region is generally used to calculate the electron-phonon coupling dominated interactions. In fact phonon self energy $\Pi(\omega)$ can be separated into adiabatic and non-adiabatic contributions [34];

$$\Pi(\omega) = \Pi^A + \Pi^{NA}(\omega) \quad (4.5)$$

Also stated in [34], that non-adiabatic calculations are extensions of the adiabatic calculation since the adiabatic one is more fundamental in a sense of presence of nuclei and electrons. They are always present, but if they also strongly interact then non-adiabatic terms are added to search for the electron-phonon coupling related quantities. Non-adiabatic calculations are then, not standalone calculations but improvements on the less accurate models.

There are also previous attempts of using electronic density as a key ingredient in spite of reaching material properties. Notable ones are Thomas-Fermi, Hartree-Fock (HF), Hartree and Slater approximations. All of them being the best of their time, they had some caveats [42]. Modern formulation is based on two sets of thoughts, Hohenberg-Kohn and Kohn-Sham Equations.

4.1 Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem, establishes a fundamental connection between the external potential of a system and its ground-state electron density. Formulated in 1964 by Pierre Hohenberg and Walter Kohn [43], this theorem provides a unique connection, revealing that the ground-state electron density uniquely determines the external potential. This theorem has immensely eased the analysis of many-electron

systems, opening a way to the DFT and in a way of thinking starting computational quantum chemistry. HK showed that electron density, at some position $\mathbf{r}$, $n(\mathbf{r})$, is enough to calculate and obtain the ground state of a N-body system. With electron density, potential is found. Using this potential, wave-function and thus the ground state is found. [44]. The problem of finding $3N$ coordinates of N atoms with 3 spatial dimensions each, reduces to finding 3 spatial coordinates of function $n(\mathbf{r})$.

The basic ideas of HK are as follows [17,39];

1. Given the ground state, the electron density $n(\mathbf{r})$ uniquely determines the external potential applied by the nuclei to the electrons.
2. If the potential is specified, in this case it is the potential of nuclei, wave-functions can be found by solving time-independent Schrodinger equation (TISE).
3. For a known quantum state the total energy is the expectation value of the Hamiltonian, so energy is also determined.

Following these calculations steps we can go from electron density to the energy of the quantum states. When electron density is changed, the energy of the system is also changed. Total energy is a functional of electron density.

4.2 Kohn-Sham Equations

HK theorem gave us the fact that ground state total energy is indeed a functional of electron density. But there is no indication how this functional will look like. The idea of Kohn and Sham was to introduce an extra energy term called *exchange and correlation energy*. As we will see later, this will come more as a problem than innovation and brings the functional dependency of DFT calculations [45]. They simplify the Schrödinger equation by approximating the many body Schrodinger equation to non-interacting single Kohn-Sham state eigenvalue equation. The Kohn-Sham equations are;

$$\left(-\nabla^2 + v_{\text{eff}}(\vec{r}) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (4.6)$$

where v_{eff} is the sum of nuclear potential, Hartree potential and new extra term exchange correlation potential. Exchange correlation potential is there for to make up for the losses of non-interacting particles approximation [17]. Modern DFT calculations that is being utilized nowadays are of this kind and named Kohn-Sham (KS) DFT [46]. Kohn-Sham equations can equivalently be described as given below for further understanding of the effective potential term;

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (4.7)$$

The first potential inside the square brackets stands $V(\mathbf{r})$ for the interaction between a single electron and some nuclei. Next potential is the Hartree potential V_H it stands for the interaction between a single Kohn-Sham state and total electron density inside the system. Since this Kohn-Sham state electron contributes to the overall charge density described above there is V_H includes the self-interaction (which is nonphysical). The last term V_{XC} stands for the exchange and correlation contributions to the independent electron Kohn-Sham equations. Actually it is kind of a correction term for all the easing approximations like independent electron approximation. V_{XC} is actually defined as functional derivative of the exchange -correlation energy, which is mathematically stated as;

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})} \quad (4.8)$$

Solving Kohn-Sham equations strictly requires to specify exchange-correlation expression. We have seen above that the Hohenberg-Kohn theorem states that exchange-correlation function must be present. But there is absolutely no indication of any kind about what the form of this functional should be [47]. One example model where the form of functional can be known is the uniform electron gas (UEG). In UEG, electron density is constant all over the space it resides in. To solve the Kohn-Sham system, we set the exchange-correlation potential to the one of the UEG at that point. Since we use the V_{XC} with each point's $n(\mathbf{r})$ we use the *local density* around position $\mathbf{r}$. Hence this method is called local density approximation (LDA). While the LDA is probably the most fundamental approach to tackle the exchange-correlation problem, there is also generalized gradient approximation (GGA). While LDA uses only the

information of the density of position $\mathbf{r}$, GGA uses the change between consecutive $\mathbf{r}$ points and contains the information of change in the electron density. Depending on how the information of derivative of the electron density is included into the GGA functional, there is a wide range of types of GGA functional. Two important ones to mention are Perdew-Wang functional (PW91) and Perdew-Burke-Ernzerhof functional (PBE) [48]. PBE functionals are also used in this study, which means we are using GGA approximation. One other class of functional is called hybrid functional. Hybrid density functional use both the exchange-correlation of our usual GGA procedure and the Hartree energy described above. How much of the Hartree energy is needed cannot be decided without real experimental results. Due to this factor they can be categorized as semi-empirical and not be considered as ab-initio.

4.3 Pseudo-potentials

Pseudo-potentials (PP) are element specific, pre-calculated tools for DFT calculations. Their purpose is to decrease the degrees of freedom involved into the calculation. If there were no PP, one has to calculate all of the nuclei orbitals of the type of atom used in calculations. Thanks to the PP calculations can approximate the nuclei potential without interacting with it. It would of course deviate from the absolute true effect of the atom, but the gain of speed and cost in calculations is superior. Even if one wants to include a more detailed model of the nuclei, the cutoff can be adjusted in that manner. Cutoff is a measure of how deep we allow the calculation to go into the core of the nuclei. For crude, for example if the valence electrons are of interest, application cutoff can be chosen to be higher, but for example in nuclear simulations where the character of atomic cores are very important then low cutoffs has to be chosen. The cutoff region can be seen in figure 4.1.

Most modern pseudo-potentials can mainly be classified under categories; norm-conserving and ultrasoft. All pseudo potentials try to replicate the all electron wavefunction after a certain distance from the atom distance, r_{cutoff} . If the pseudopotential and the all electron function share the same amount of charge inside the cutoff distance the PP is said to be norm-conserving, given mathematically [49];

$$Q_l = \int_0^{R_c} dr r^2 |\psi_l(r)|^2 = \int_0^{R_c} dr \phi_l(r)^2, \quad (4.9)$$

where $\psi_l(r)$ is the all-electron wavefunction for orbital l and $\phi_l(r)$ is the pseudo-wavefunction. This conservation keeps the amount of charge in the nuclei (inside the cutoff distance) same as the real material. This property increases the ability of PP's transferability. This property of transferability enables one to use the PP in many other chemical combinations from the first configuration the where the PP is created for. PP's ability to replicate the ionic configuration (nuclei) of the real atom is generally named as "hardness" of the potential. These hard potentials generally require higher cutoff energies. Hard PPs also generally have sharper peaks. Whereas if the PP is more application-oriented and fine-tuned in the valence electrons' region, it is called "soft" pseudo-potential. Soft potentials are computationally more efficient relative to the hard potentials. Next type of PP is called ultrasoft (USSP). As we defined the meaning of soft, ultrasoft potentials require really low cutoff energies compared to the other PP families. One disadvantage of USSPs are they require some amount of empirical parameters [48]. Ultrasoft PPs are divided into two parts a smooth and soft valence electron part and a more bumpy and hard core structure part. This time norm-conservation condition is not satisfied for the core part.

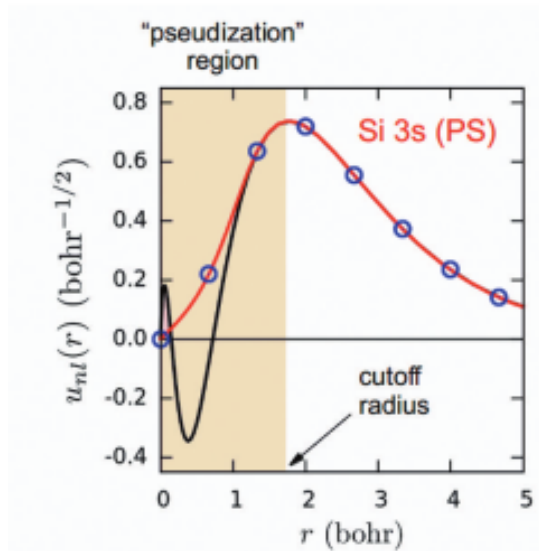


Figure 4.1 : Pseudo-potential in action. The black curve represents the real wave-function form in real space. Red curve shows the calculated pseudo potential for the orbital. [17].

4.4 Quantum Espresso Software

Quantum ESPRESSO (QE) is an open-source software suite that performs electronic structure calculations based on density functional theory (DFT). It is used to simulate and understand the quantum mechanical behavior of materials. The code enables self-consistent field calculations to determine the ground-state electronic structure. It can calculate geometry optimizations to find the stable configuration of atoms in a crystal lattice, and runs molecular dynamics simulations to study the dynamic behavior of materials. QE also computes vibrational properties, such as phonon frequencies and mode shapes, providing dispersion relations of lattice vibrations and thermal properties. It can also analyze band structures, density of states, and various post-processing capabilities.

4.4.1 Vc-relax & relax

vc-relax calculation is step for optimizing the structure of given unit cell. By using this program one can achieve the most stable cell parameters with given inputs. The flow of the program starts with computer making an initial guess for the cell dimensions. Then a self-consistent calculation is run to check the electronic ground state. After the self-consistent calculation program checks for the stress, energy and forces thresholds to see if the structure is within the limits. This procedure goes on until the threshold convergence is achieved. For the relax calculation, this time the atomic positions are the candidate for initial guesses. Inside the determined cell structure the same subroutines apply to atomic positions the optimum locations. Sample input files for this operation is given in listings A.1 and A.2

4.4.2 Scf

In self-consistent field (scf) calculations the aim is to calculate the electronic wavefunctions and charge density. An initial guess is used to solve Kohn-Sham equations. After that cell dimensions and atomic positions are again changed but this time they are finely tuned. Sample input file for this operation is given in listing A.3

4.4.3 Nscf

After scf calculation is done, a non-scf calculation starts. Charge density is now known thanks to the scf calculation. nscf uses this charge density values to calculate Kohn-Sham states, compute the density of states. Sample input file for this operation is given in listing A.4

4.4.4 Bands, bands-pp

The resulting graph for electronic band structure is given in figures 4.2 and 4.3. Figure 4.2 is created using the Quantum Espresso software bands, where the latter figure 4.3 is created by Wannier90 software. Following both ways for the electronic band structure calculations is a good way to check the obtained data for the material studied. Sample input files for these operations are given in listings A.5, A.6 and A.7

4.4.5 Ph, q2r, matdyn

ph.x program calculates the vibrational properties of the lattice given. More specifically it calculates normal modes at specific $\mathbf{q}$ vectors taken as inputs. Finally it prints out the dynamical matrix files of the system. q2r takes this dynamical matrix files and calculates the force constant between the components of the grid. Finally, matdyn finally calculates the phonon frequencies needed for the phonon dispersion plots. Resulting phonon graph is given in figure 4.7. In fig 4.8 phonon bands are colored according to their band index ν . Sample input files for these operations are given in listings A.8, A.9 and A.10

4.4.6 Plotband

plotband is a small program to transform the calculated atomic properties into several file formats for better and easier plotting. Sample input file for this operation is given in listing A.11

4.4.7 EPW

EPW code calculates the electron-phonon related parameters using density functional perturbation theory and maximally localized wannier functions. Two files have been used for the calculations. First epw file is needed to calculate the tight-binding matrix.

Second file is for the calculation needed. We needed g_{kk} values so in second file we have opened the prtgkk parameter and ran the epw.x program again. Sample input file for this operation is given in listing A.12. Second input file is given in listing A.13.

4.4.8 Wannier90

Wannier90 (W90) is a computational code used in condensed matter physics to transform electronic wave-functions from a material's Bloch states to localized Wannier functions. These functions provide a more intuitive and efficient description of electronic structure, facilitating the study of various physical phenomena. Wannier90 aids in understanding complex materials by generating maximally localized Wannier functions, this enables us to analyze electronic properties, calculate transport characteristics, and investigate novel quantum states. The code is very important in bridging the gap between ab-initio electronic structure calculations and model Hamiltonians, making it a valuable tool for predicting and interpreting the behavior of materials at the atomic and electronic levels. The ab-initio codebase we use in this work is QE. W90 should be used after the QE's scf and nscf calculations with an intermediate program, pw2wannier90.x. Main wannier file used during the calculations is given in listing A.14. The electronic bands calculated this way is given in figure 4.3. The Fermi surface of the material is plotted using the Band XSF files given by the W90 output and XCRYSDEN program, the resultant figures are given in 4.10, 4.4 and 4.11.

4.5 Computational Details

For the Niobium element, PBE (GGA) functional, USPP type potentials are used. For the Selenium, PBE (GGA) exc-corr functional, non-relativistic, norm-conserving pseudopotentials are used. For the electronic structure k-mesh size is $16 \times 16 \times 1$. For the lattice (phonon) structure we have $8 \times 8 \times 1$. For the EPW mesh of $24 \times 24 \times 1$ is used for both k and q meshes.

4.6 Results

The first graph we have calculated is the electronic band structure diagram of the material NbSe₂. The result is given in Fig. 4.2. The same result is then calculated again using maximally localized Wannier functions by using the code Wannier90 in Fig. 4.3.

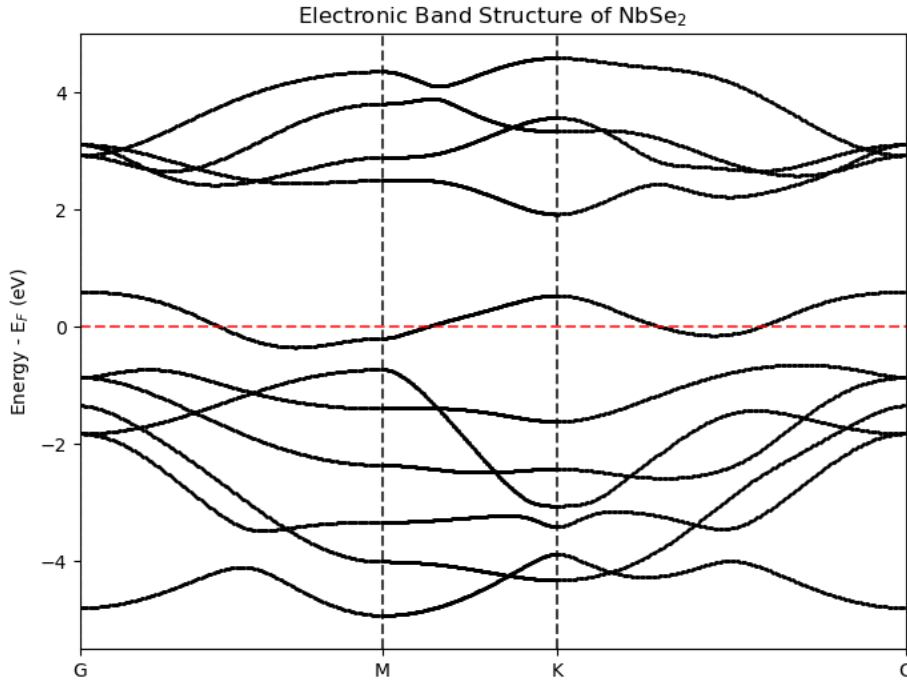


Figure 4.2 : Electronic bands on the path Γ MK Γ . Calculated using QE (PWscf) code.

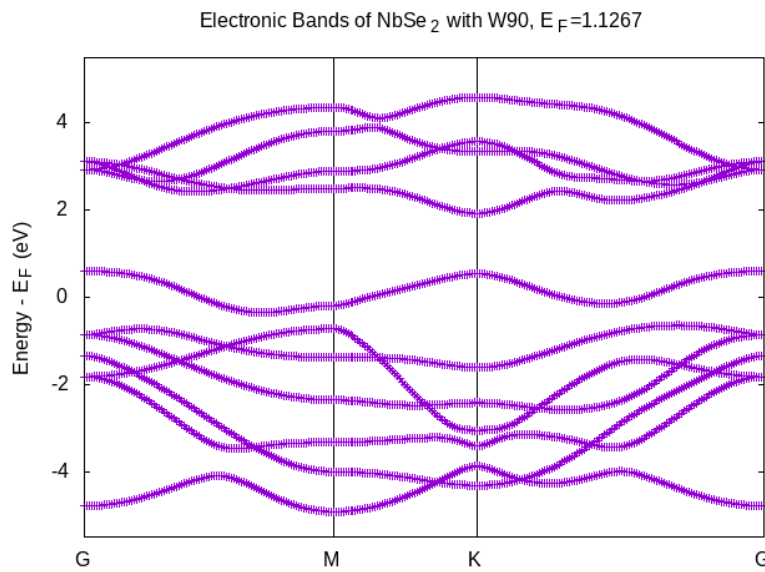


Figure 4.3 : Electronic bands on the path Γ MK Γ . Calculated using Wannier90 code.

The reciprocal unit cell of the NbSe₂ is given in Fig. 4.4. This graph is acquired using the output data of Wannier90 code process and feeding that output into the XcrysDen software.

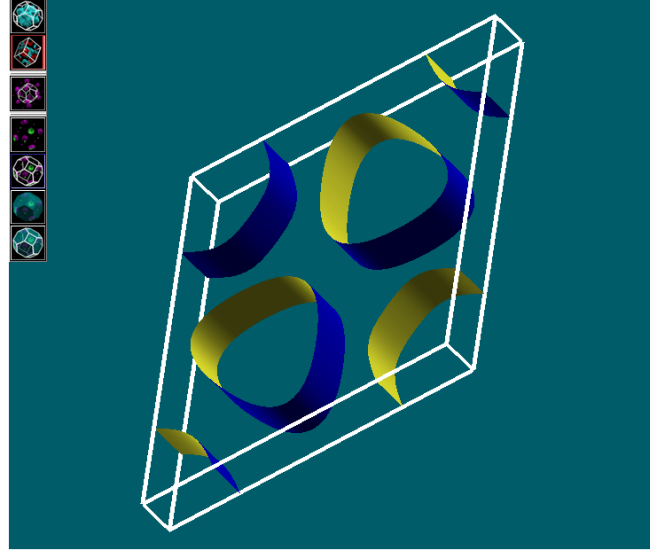


Figure 4.4 : Fermi surface of 1H-NbSe₂ drawn inside the reciprocal unit cell.

The phonon diagrams show an evolution as the degauss parameter σ is changed. degauss parameter is commonly called the electronic temperature and simulates the effect of usual temperature. What it does computationally is to ease the numerical convergence of states around the Fermi level. The evolution of the graphs as the σ value decreases is given in Figs. 4.5, 4.6 and 4.7.

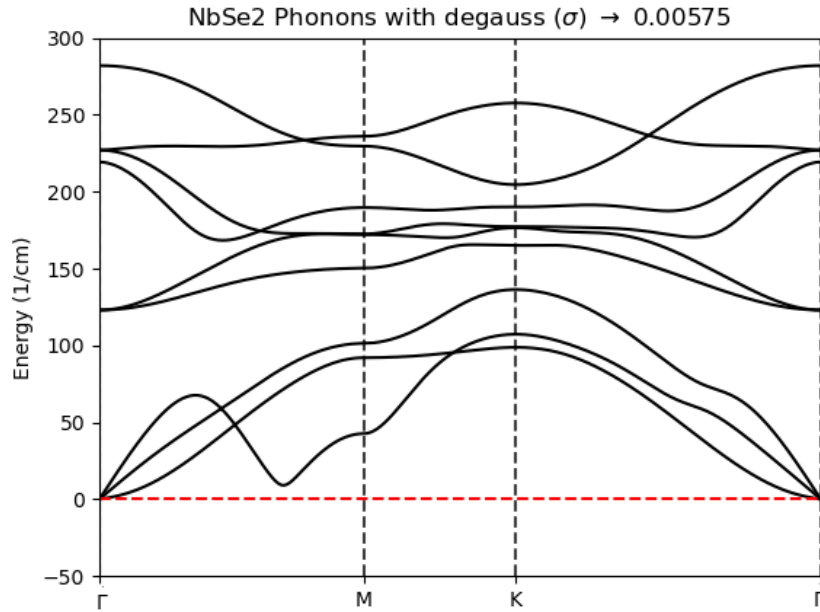


Figure 4.7 : Phonon dispersion bands on the path Γ MK Γ .

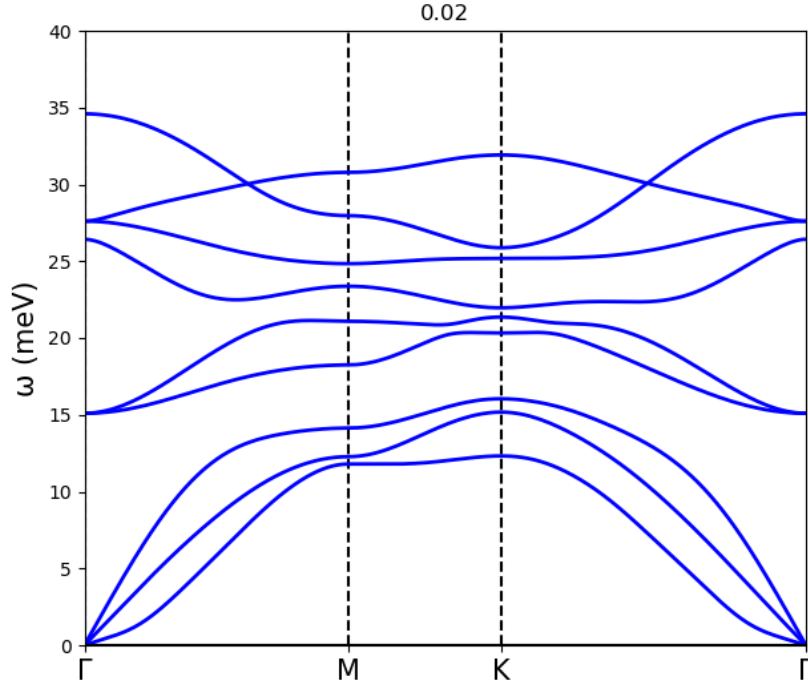


Figure 4.5 : Phonon diagram for smearing value σ of 0.02. No visible distortions in the acoustic phonon bands for this parameter

In Fig 4.9, the band depicting the Kohn anomaly phenomena is colored. The coloring is achieved via a simple script. The phonon bands versus q-point values are given in two huge columns where only x and y values are present. There is no band character or whatsoever. We go over this data to extract the values for a single band. A numerical loop goes over the data, if at a single q-value, two phonon frequency value is present loop checks the previous and the incoming data points to determine if the crossing frequency point belongs to a band behavior.

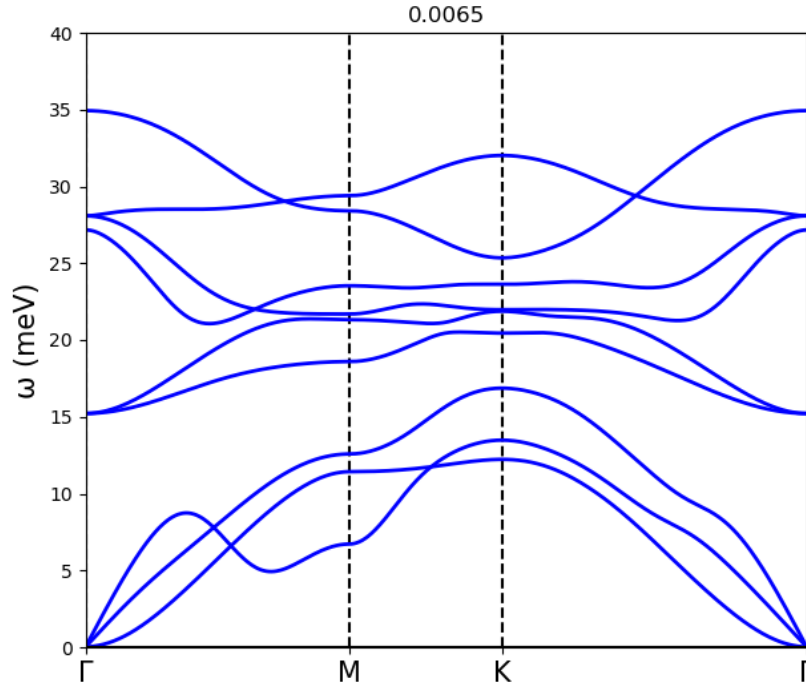


Figure 4.6 : Phonon diagram for smearing value σ of 0.0065. One of the acoustic phonon band start to approach lower energies.

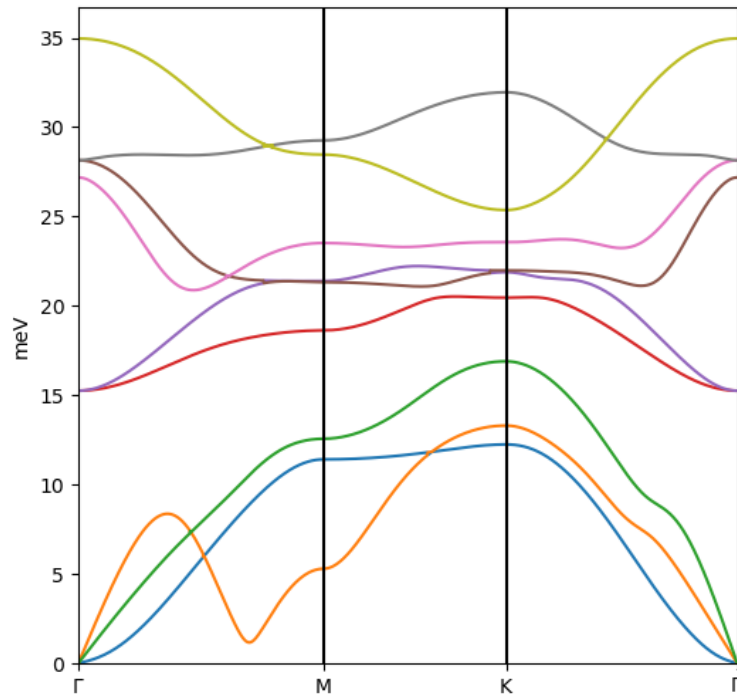


Figure 4.8 : Untangled phonon band. Phonon bands are colored according to their band index ν

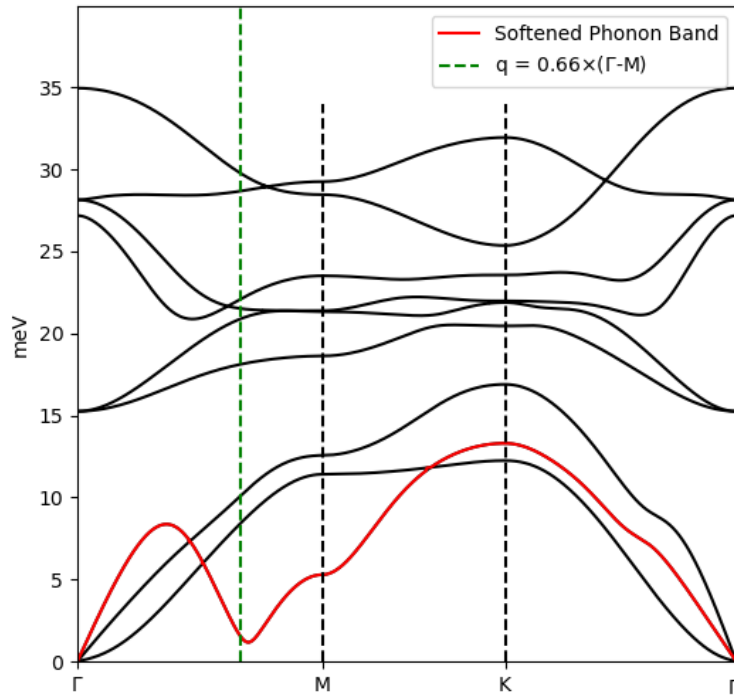


Figure 4.9 : Untangled phonon bands. Only softened phonon band is colored for display of Kohn anomaly.

In Figures 4.10 and 4.11 the Fermi surface of the material 1H-NbSe₂ is generated. The Fermi surface data is important for the study since for the Fermi surface nesting we need to calculate the nesting density on the whole Fermi Surface. The 3D image is generated using the Wannier90 output files, and visualizing them on XcrysDen program.

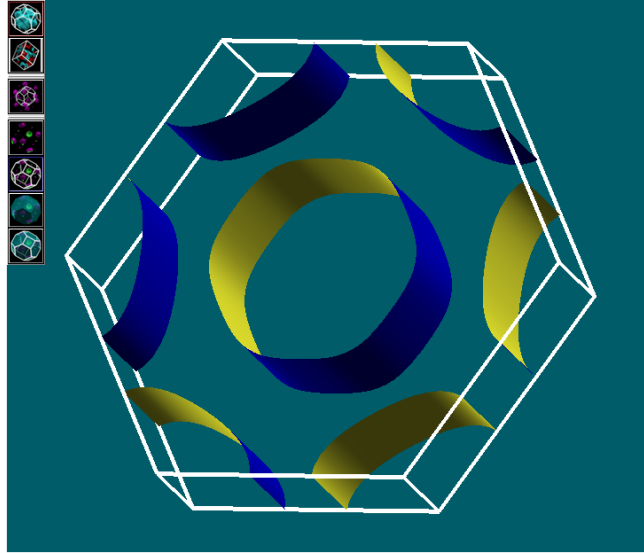


Figure 4.10 : Fermi surface of 1H-NbSe₂ drawn inside the Brillouin zone.

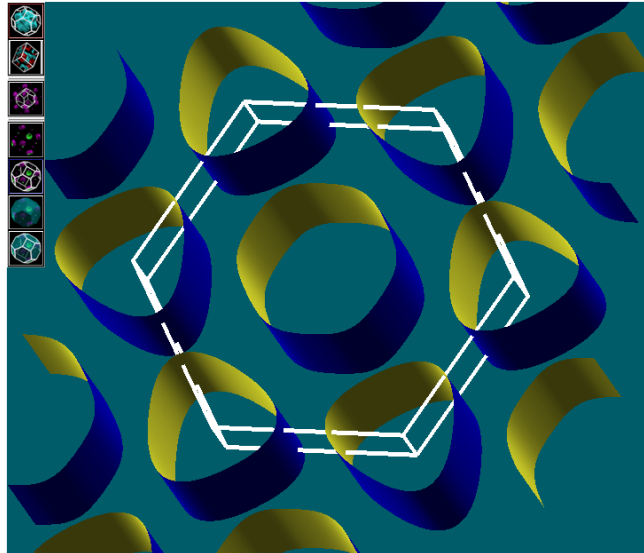


Figure 4.11 : Fermi surface of 1H-NbSe₂ drawn in reciprocal space but not bounded by the BZ and plotted also on the neighboring cells.

The susceptibility data are given in Figures 4.12, 4.13 and 4.14. The Figure 4.12 shows the susceptibility drawn on the selected high symmetry points path. It can be visualized as the triangular path in Figure 3.8 in a flattened way. Data in this graph is obtained by directly calculating the Lindhard susceptibility using the Fermi-Dirac functions and energies in a numerical loop. One can see that there is a relative peak about $\mathbf{q} = 2/3 (\Gamma - \mathbf{M})$ but it's effectiveness will be discussed later in the conclusion. In the latter figures 4.13 and 4.14 ,the the susceptibility is drawn into the pieces of the Brillouin zone. Since the large mesh requires heavy computational power, first the data in Figure 4.14 is obtained and the Figure 4.13 is obtained by rotating it around the center Γ point. This is a legit way since the BZ in hand has 60 degrees rotations symmetry.

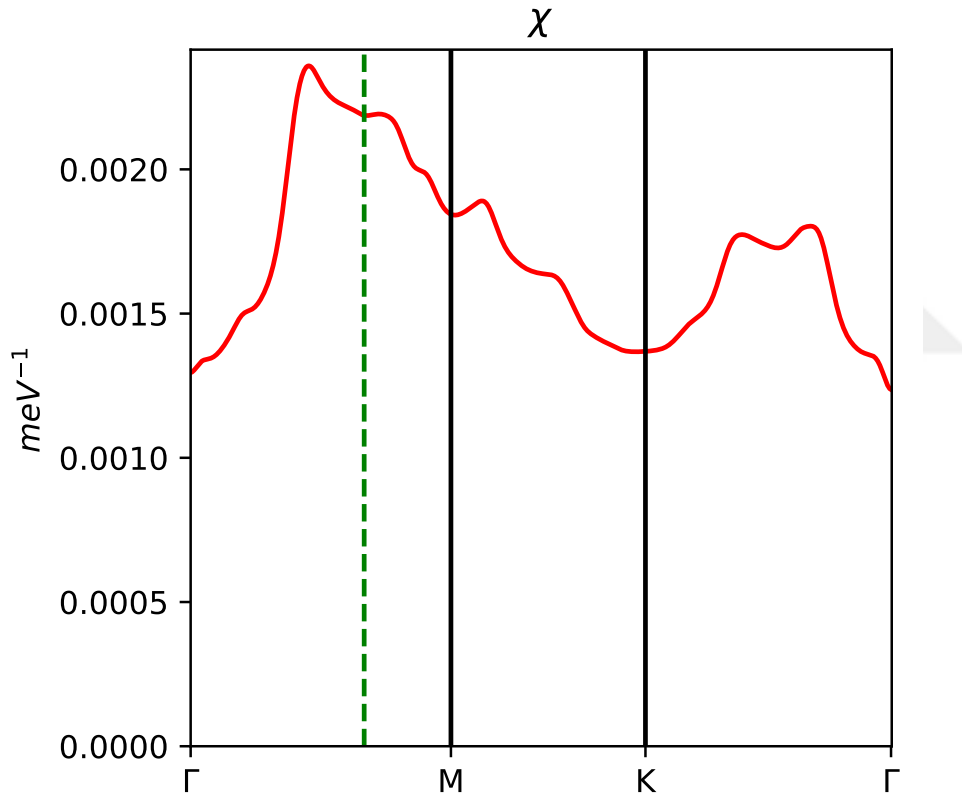


Figure 4.12 : $\chi'_{\mathbf{q}}$, static Linhard susceptibility. It's peaks indicate that in those $\mathbf{q}$ points there can be a instability. Green dashed line shows the $\mathbf{q} = 2/3 (\Gamma - \mathbf{M})$. The peak around the green dashed line has peak behavior of %38. It goes 3.8 times above the average value of the data.

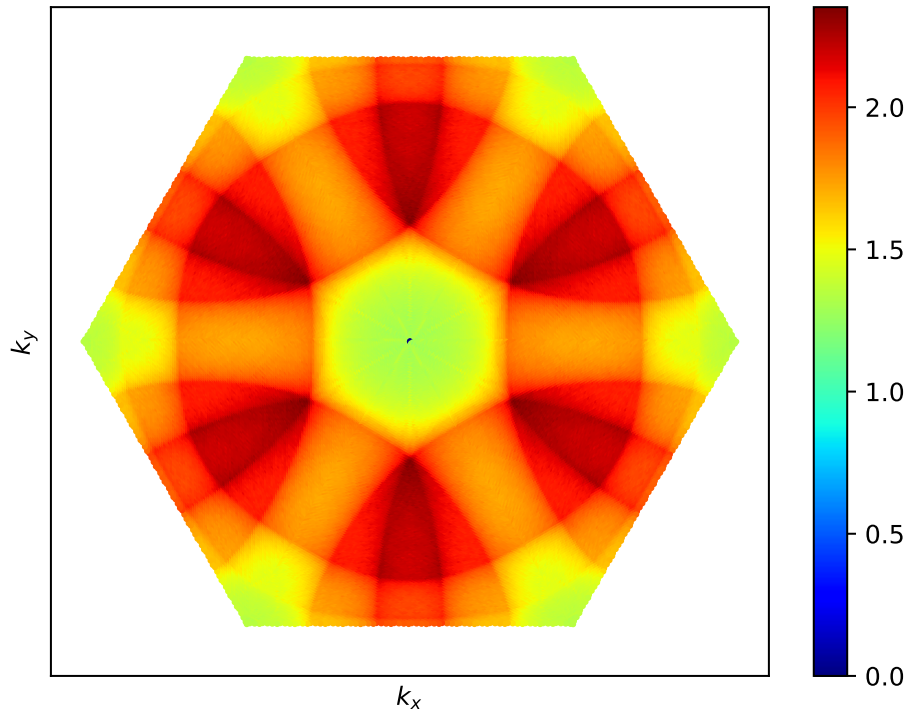


Figure 4.13 : Susceptibility drawn onto the Brillouin zone of the material. There are no sharp peak points but more like flat plateaus. This indicates that susceptibility is not immensely effective in instability formation.

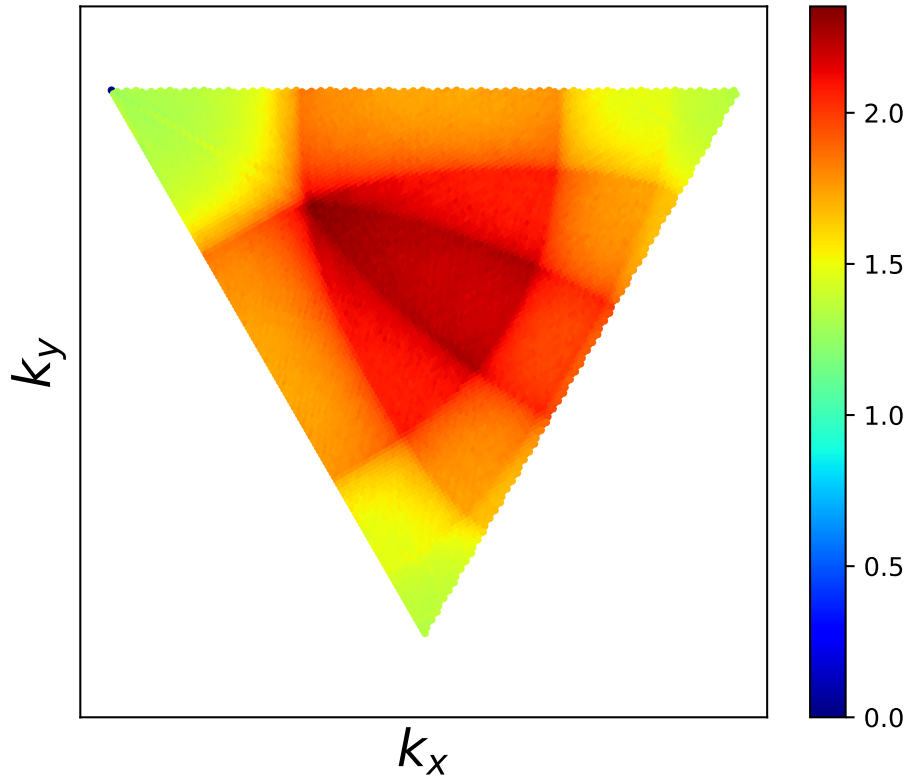


Figure 4.14 : Susceptibility drawn into the Γ MK Γ path, also k-path zone has mirror symmetry around Γ -M line.

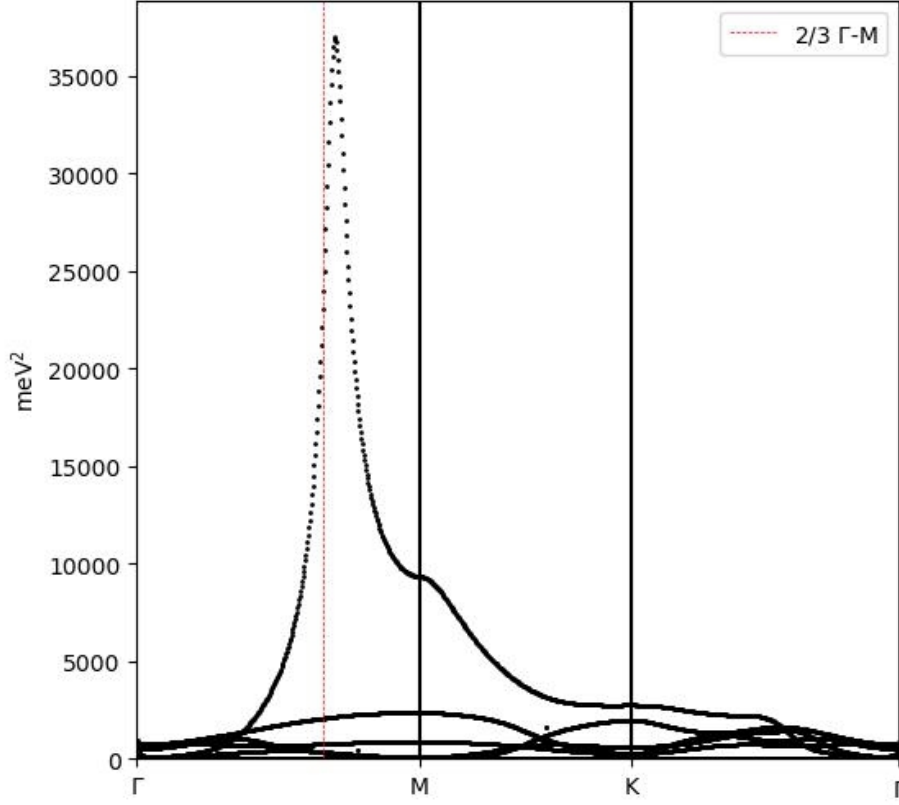


Figure 4.15 : q -dependent electron-phonon coupling constant $g_{q,\lambda}$. The peak goes above 8.65 times the average of data. There is %865 peak behavior.

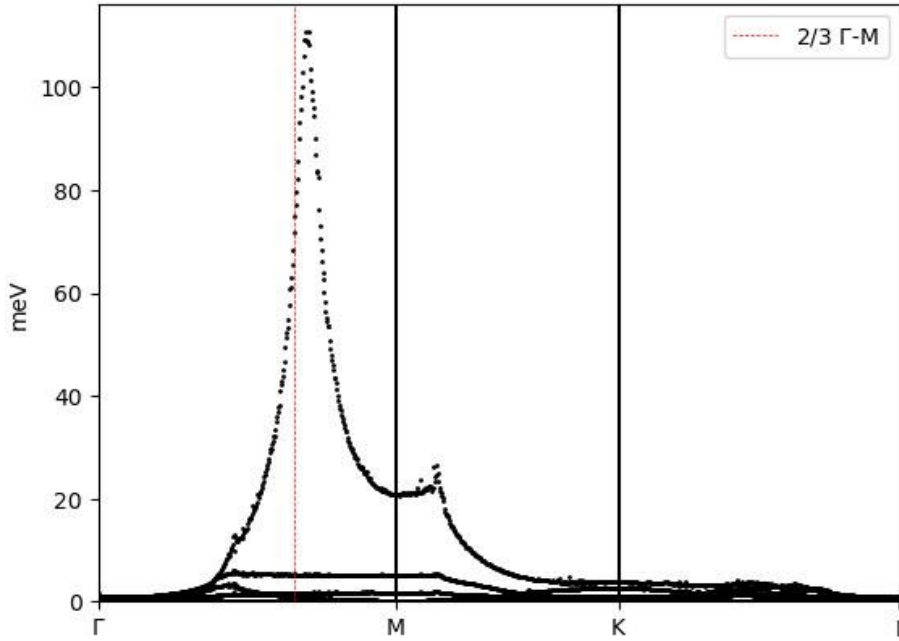


Figure 4.16 : Phonon self energy. At the $\mathbf{q}_{CDW} = 2/3(\Gamma - M)$ phonon self energy is very large and peaked. This indicates high electron phonon coupling activity in $\mathbf{q}_{CDW}$.

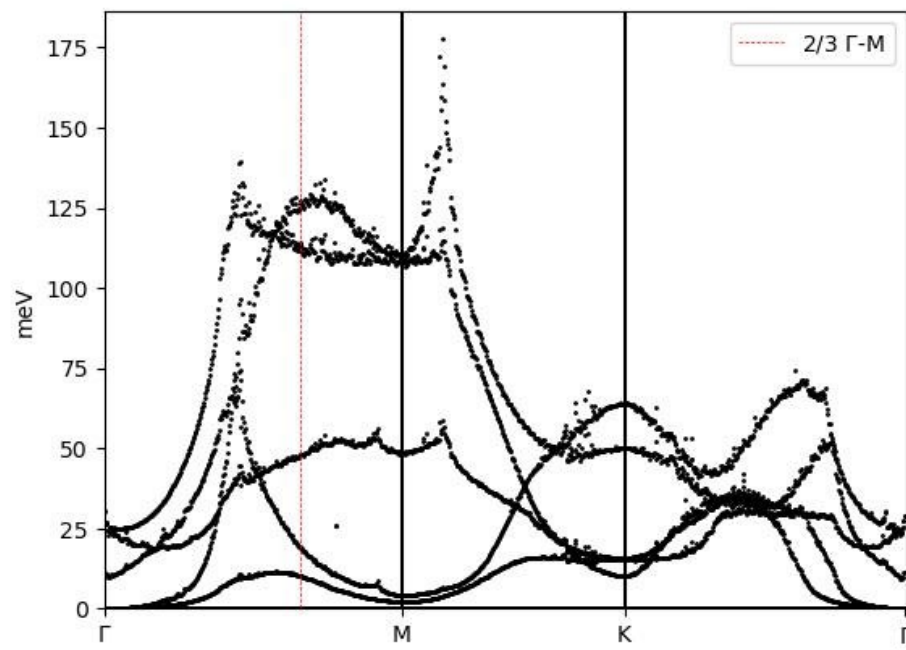


Figure 4.17 : Diagonal elements of self energy matrix



5. CONCLUSION

Calculated phonon self energy in figure 4.16 shows that there is very high electron-phonon contribution around $\mathbf{q}_{\text{CDW}}$. Phonon self energy has contributions from both momentum dependent electron coupling constant squared $\bar{g}_{\mathbf{q},\lambda}$ and static Lindhard susceptibility $\chi'_{\mathbf{q}}$ drawn in figure 4.12. If we compare $\bar{g}_{\mathbf{q},\lambda}$ (figure 4.15) and phonon self energy we can see there is a high resemblance between them. Whereas if we compare phonon self energy and static Lindhard susceptibility, we cannot see much of a similarity. This tells us $\mathbf{q}$ -EPC is dominant in CDW instability formation. Also, found data is consistent with the literature data given in figure 2.11.

Firstly, we will compare figure 2.11 (a) with $\chi'_{\mathbf{q}}$ in figure 4.12. For the BZ plots of figure 2.11 the center of the hexagon is the Γ point and the top side of the hexagon is M point. So we should check for similarities in $\Gamma - M$ region. Behavior of our data exactly matches with the BZ graphs of figure 2.11.

Same thing is applicable for also the $\bar{g}_{\mathbf{q},\lambda}$ in fig 4.15 and graph in 2.11 (b). At the same point the graphs have a peak, which is also very close $\mathbf{q}_{\text{CDW}}$. we can definitely say that $\mathbf{q}$ -EPC is dominant in material NbSe₂. It is also pointed out that $\mathbf{q}$ -EPC is dominant in NbSe₂ for CDW formation in [9]

Despite not dominant in the CDW formation of our material, our calculated susceptibility figure 2.5 can be compared to figure 2.11(a) for reference. The rates of change on the middle of the $\Gamma - M$ path is very close and the behavior of the data is very similar.

On the other hand, Fermi surface nesting may be effective but not dominant since in figure 4.12, there is no peaks sticking out of the general trend of data. For the peaks if we try to quantify them, we can measure how much they elevate from their datasets' respective mean value. For the electron-phonon coupling descriptor $\bar{g}_{\mathbf{q},\lambda}$ the values for peak behavior is %865, which means the top of the peak is 8,65 times bigger than the mean value in terms of meV². The value for the other candidate Fermi surface

nesting, hence the susceptibility is %38 means that the peak is 0.38 times bigger than the average value in terms of meV^{-1} . It is clear that electron-phonon coupling has more significant effect on the instability.



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APPENDICES

APPENDIX A : INPUT FILES FOR DFT SOFTWARE & SCRIPTS

APPENDIX B : DERIVATION FOR KOHN-SHAM EQUATIONS





APPENDIX A - INPUT FILES FOR DFT SOFTWARE & SCRIPTS

Listing A.1 : Sample file for vc-relax input.

```
1 &CONTROL
2 etot_conv_thr = 1d-06
3 forc_conv_thr = 1d-05
4 prefix       = '0.00575'
5 calculation   = 'vc-relax'
6 outdir        = './outdir'
7 pseudo_dir    = '../pseudos/'
8 tprnfor       = .true.
9 tstress       = .true.
10 /
11 &SYSTEM
12 degauss      = 0.00575
13 ecutwfc      = 200
14 ecutrho      = 800
15 ibrav        = 0
16 nat          = 6
17 ntyp         = 2
18 occupations  = 'smearing'
19 smearing     = 'fd'
20 /
21 &ELECTRONS
22 conv_thr     = 1d-12
23 mixing_mode  = 'local-TF'
24 /
25 &IONS
26 /
27 &CELL
28 /
29 ATOMIC_SPECIES
30 Nb 92.90 Nb.pbe-spn-rrkjus_psl.1.0.0.UPF
31 Se 78.96 Se.pbe-mt_fhi.UPF
32 ATOMIC_POSITIONS (crystal)
33 Nb 0.0000000000 0.0000000000 0.2500000000
34 Nb -0.0000000000 -0.0000000000 0.7500000000
35 Se 0.6666666667 0.3333333333 0.6284242986
36 Se 0.3333333333 0.6666666667 0.1284242986
37 Se 0.6666666667 0.3333333333 0.8715757014
38 Se 0.3333333333 0.6666666667 0.3715757014
39 CELL_PARAMETERS (angstrom)
40 3.479732015 0.0 0.0
```

```

41 -1.739866009 3.013536323 -0.0
42 -0.0 0.0 13.819198288
43 K_POINTS automatic
44 20 20 10 0 0 0

```

Listing A.2 : Sample file for relax input.

```

1 &CONTROL
2 etot_conv_thr = 1d-06
3 forc_conv_thr = 1d-05
4 prefix       = '0.00575'
5 calculation   = 'relax'
6 outdir        = './outdir'
7 pseudo_dir    = '../pseudos/'
8 tprnfor       = .true.
9 tstress       = .true.
10 /
11 &SYSTEM
12 degauss      = 0.00575
13 ecutwfc      = 200
14 ecutrho      = 800
15 ibrav        = 0
16 nat          = 3
17 ntyp         = 2
18 occupations  = 'smearing'
19 smearing     = 'fd'
20 /
21 &ELECTRONS
22 conv_thr     = 1d-12
23 mixing_mode  = 'local-TF'
24 /
25 &IONS
26 /
27 &CELL
28 /
29 ATOMIC_SPECIES
30 Nb 92.90 Nb.pbe-spn-rrkjus_psl.1.0.0.UPF
31 Se 78.96 Se.pbe-mt_fhi.UPF
32 ATOMIC_POSITIONS (crystal)
33 Nb 0.0 0.0 0.5
34 Se 0.3333333333 0.6666666667 0.37842753149999997
35 Se 0.3333333333 0.6666666667 0.6215724684999999
36 CELL_PARAMETERS (angstrom)
37 3.479745245 0.0 -0.0
38 -1.739872624 3.01354778 -0.0
39 0.0 0.0 13.819586475
40 K_POINTS automatic
41 20 20 1 0 0 0

```

Listing A.3 : Sample file for scf input.

```

1 &CONTROL
2   etot_conv_thr = 1d-06
3   forc_conv_thr = 1d-05
4   prefix        = '0.00575'
5   calculation    = 'scf'
6   outdir         = './'
7   pseudo_dir     = './pseudos/'
8   tprnfor        = .true.
9   tstress        = .true.
10  /
11 &SYSTEM
12   degauss       = 0.00575
13   ecutwfc       = 200
14   ecutrho       = 800
15   ibrav         = 0
16   nat           = 3
17   ntyp          = 2
18   occupations   = 'smearing'
19   smearing      = 'fd'
20  /
21 &ELECTRONS
22   conv_thr      = 1d-12
23   mixing_mode   = 'local-TF'
24  /
25 &IONS
26  /
27 &CELL
28  /
29 ATOMIC_SPECIES
30 Nb 92.90 Nb.pbe-spn-rrkjus_psl.1.0.0.UPF
31 Se 78.96 Se.pbe-mt_fhi.UPF
32 ATOMIC_POSITIONS (crystal)
33 Nb 0.0000000000 0.0000000000 0.5000000000
34 Se 0.3333333333 0.6666666667 0.3784226732
35 Se 0.3333333333 0.6666666667 0.6215773268
36 CELL_PARAMETERS (angstrom)
37 3.479745245 0.0 -0.0
38 -1.739872624 3.01354778 -0.0
39 0.0 0.0 13.819586475
40 K_POINTS automatic
41 16 16 1 0 0 0

```

Listing A.4 : Sample file for nscf input.

```

1 &CONTROL
2   etot_conv_thr = 1d-06
3   forc_conv_thr = 1d-05
4   prefix = '0.00575'

```

```

5  calculation = 'bands'
6  outdir = './'
7  pseudo_dir = './pseudos/'
8  tprnfor = .true.
9  tstress = .true.
10 /
11 &SYSTEM
12  degauss      = 0.00575
13  ecutwfc      = 200
14  ecutrho      = 800
15  ibrav       = 0
16  nat         = 3
17  ntyp        = 2
18  occupations  = 'smearing'
19  smearing     = 'fd'
20  !nosym=.TRUE.
21  nbnd = 17
22 /
23
24 &ELECTRONS
25  conv_thr     = 1d-12
26  mixing_mode  = 'local-TF'
27 /
28
29 &IONS
30 /
31
32 &CELL
33 /
34
35 ATOMIC_SPECIES
36 Nb 92.90 Nb.pbe-spn-rrkjus_psl.1.0.0.UPF
37 Se 78.96 Se.pbe-mt_fhi.UPF
38
39 ATOMIC_POSITIONS (crystal)
40 Nb 0.0000000000 0.0000000000 0.5000000000
41 Se 0.3333333333 0.6666666667 0.3784226732
42 Se 0.3333333333 0.6666666667 0.6215773268
43 CELL_PARAMETERS (angstrom)
44 3.479745245 0.0 -0.0
45 -1.739872624 3.01354778 -0.0
46 0.0 0.0 13.819586475
47 K_POINTS crystal
48 256
49 0.00000000 0.00000000 0.00000000 3.906250e-03
50 0.00000000 0.06250000 0.00000000 3.906250e-03
51 0.00000000 0.12500000 0.00000000 3.906250e-03
52 ...

```

Listing A.5 : Sample file for dos input.

```

1 &DOS
2   prefix='0.0057',
3   outdir='./',
4   fildos='0.0057_dos.dat',
5   emin=-6.0,
6   emax=7.0
7 /

```

Listing A.6 : Sample file for bands input.

```

1
2 &CONTROL
3 etot_conv_thr = 1d-06
4 forc_conv_thr = 1d-05
5 prefix        = '0.0057'
6 calculation    = 'bands'
7 outdir         = './'
8 pseudo_dir     = '../pseudos/'
9 tprnfor        = .true.
10 tstress       = .true.
11 /
12 &SYSTEM
13 degauss       = 0.0057
14 ecutwfc       = 100
15 ecutrho       = 800
16 ibrav         = 0
17 nat           = 3
18 ntyp          = 2
19 occupations   = 'smearing'
20 smearing      = 'fd'
21 /
22 &ELECTRONS
23 conv_thr      = 1d-12
24 mixing_mode   = 'local-TF'
25 /
26 &IONS
27 /
28 &CELL
29 /
30 ATOMIC_SPECIES
31 Nb 92.90 Nb.pbe-spn-rrkjus_psl.1.0.0.UPF
32 Se 78.96 Se.pbe-mt_fhi.UPF
33 ATOMIC_POSITIONS (crystal)
34 Nb 0.0000000000 0.0000000000 0.5000000000
35 Se 0.3333333333 0.6666666667 0.3784194563
36 Se 0.3333333333 0.6666666667 0.6215805437
37 CELL_PARAMETERS (angstrom)
38 3.479732015 0.0 0.0

```

```

39 -1.739866009 3.013536323 -0.0
40 -0.0 0.0 13.819198288
41 K_POINTS crystal_b
42 4
43 0 0 0 200 ! G
44 0 0.5 0 200 ! M
45 0.3333333 0.3333333 0 200 ! K
46 0 0 0 200 ! G

```

Listing A.7 : Sample file for bands-pp input.

```

1 &bands
2 outdir = './'
3 prefix = '0.0057'
4 filband = 0.0057.bands.dat
5 /

```

Listing A.8 : Sample file for ph input.

```

1 &inputph
2 prefix = '0.00575'
3 fildyn = './0.00575.dyn',
4 outdir = './'
5 ldisp = .true.,
6 trans = .true.,
7 fildvscf = 'dvscf',
8 nq1 = 8,
9 nq2 = 8,
10 nq3 = 1,
11 tr2_ph = 1d-16,
12 /

```

Listing A.9 : Sample file for q2r input.

```

1 &input
2 fildyn = './0.00575.dyn',
3 zasr = 'simple'
4 flfrc = './0.00575.fc'
5 /

```

Listing A.10 : Sample file for matdyn input.

```

1 &input
2 asr = 'simple'
3 flfrc = './0.00575.fc'
4 flfrq = './0.00575.freq'
5 q_in_band_form=.true.
6 q_in_cryst_coord=.true.
7 /
8 4
9 0 0 0 200 ! G

```

```

10 0 0.5 0 200 ! M
11 0.3333333 0.3333333 0 200 ! K
12 0 0 0 200 ! G

```

Listing A.11 : Sample file for plotband input.

```

1 0.00575.freq
2 0 550
3 0.00575.xmgr

```

Listing A.12 : Sample file for epw input.

```

1 --
2 &inputepw
3   prefix      = '0.00575',
4   amass(1)    = 92.90,
5   amass(2)    = 78.96,
6   outdir      = './',
7   dvscf_dir   = './save',
8
9   elph        = .true.
10  !kmaps      = .false.
11  epbwrite     = .true.
12  epbread     = .false.
13  epwwrite    = .true.
14  epwread     = .false.
15
16  wannierize   = .true.
17  nbndsub     = 11
18
19  fermi_energy = 1.1267
20  efermi_read = .true.
21
22
23  num_iter     = 2000
24  dis_win_max  = 10
25  dis_win_min  = -10
26  dis_froz_min = 0.6
27  dis_froz_max = 2
28  proj(1)     = 'Nb:d'
29  proj(2)     = 'Se:p'
30  wdata(1)    = 'bands_plot = .true.'
31  wdata(2)    = 'begin kpoint_path'
32  wdata(3)    = 'G 0.00 0.00 0.00 M 0.00 0.50 0.00'
33  wdata(4)    = 'M 0.00 0.50 0.00 K 0.33 0.33 0.00'
34  wdata(5)    = 'K 0.33 0.33 0.00 G 0.00 0.00 0.00'
35  wdata(6)    = 'end kpoint_path'
36  wdata(7)    = 'bands_num_points = 100'
37
38  elecselken  = .false.

```

```

39 phonselfen = .false.
40 a2f        = .false.
41
42 fsthick     = 0.65 ! eV
43 temps      = 2 ! K
44 degaussw    = 0.05 ! eV
45
46 nkf1        = 24
47 nkf2        = 24
48 nkf3        = 1
49 nqf1        = 24
50 nqf2        = 24
51 nqf3        = 1
52
53 nk1         = 16
54 nk2         = 16
55 nk3         = 1
56 nq1         = 8
57 nq2         = 8
58 nq3         = 1
59 /

```

Listing A.13 : Sample file for the second epw input.

```

1 --
2 &inputepw
3 prefix      = '0.00575',
4 amass(1)    = 92.90,
5 amass(2)    = 78.96
6 outdir      = './'
7 dvscf_dir   = './save'
8
9 elph        = .true.
10 !kmaps      = .true.
11 epbwrite    = .false.
12 epbread     = .false.
13 epwwrite    = .true.
14 epwread     = .false.
15
16 wannierize  = .false.
17 nbndsub     = 11
18
19 efermi_read = .true.
20 fermi_energy = 1.1267
21
22
23
24 elecsselfen = .false.
25 phonsselfen = .true.

```

```

26  delta_approx= .true.
27  a2f          = .false.
28  band_plot    = .false.
29  prtggk       = .true.
30
31
32  fsthick       = 0.7
33  temps         = 2
34  degaussw      = 0.00575
35  eps_acustic   = 0.005
36  filqf="./GMKG_1001.path".
37
38
39  nkf1          = 128
40  nkf2          = 128
41  nkf3          = 1
42  ! nqf1        = 1
43  ! nqf2        = 1
44  ! nqf3        = 1
45
46  nk1           = 16
47  nk2           = 16
48  nk3           = 1
49  nq1           = 8
50  nq2           = 8
51  nq3           = 1
52  /

```

Listing A.14 : Sample file for wannier90 input.

```

1  num_bands = 17
2  num_wann = 11
3
4  dis_win_min = -10
5  dis_win_max = 10
6
7  dis_froz_min = -0.6
8  dis_froz_max = 1
9
10 write_hr=T
11
12 guiding_centres=T
13
14 Begin Projections
15 Nb:d
16 Se:p
17 End Projections
18
19 kpath = true

```

```

20 kpath_task = bands
21 kpath_num_points=1000
22 bands_plot = true
23
24 begin unit_cell_cart
25 3.479732015 0.0 0.0
26 -1.739866009 3.013536323 -0.0
27 -0.0 0.0 13.819198288
28 end unit_cell_cart
29
30 begin atoms_frac
31 Nb 0.0000000000 0.0000000000 0.5000000000
32 Se 0.3333333333 0.6666666667 0.3784194563
33 Se 0.3333333333 0.6666666667 0.6215805437
34 end atoms_frac
35
36 begin kpoint_path
37 G 0.000 0.000 0.000 M 0.000 0.500 0.000
38 M 0.000 0.500 0.000 K 0.333 0.333 0.000
39 K 0.333 0.333 0.000 G 0.000 0.000 0.000
40 end kpoint_path
41
42 mp_grid = 16 16 1
43 begin kpoints
44 0.00000000 0.00000000 0.00000000 3.906250e-03
45 0.00000000 0.06250000 0.00000000 3.906250e-03
46 0.00000000 0.12500000 0.00000000 3.906250e-03
47 ...
48 end kpoints

```

Listing A.15 : Sample slurm script to run the calculations on TRUBA cluster

```

1 #!/bin/bash
2 #SBATCH -M truba
3 #SBATCH -p hamsi
4 #SBATCH -A csanga
5 #SBATCH -J thesis575
6 #SBATCH -N 2
7 #SBATCH -n 56
8 #SBATCH --time=3-00:00:00
9 #SBATCH --output=slurm-%j.out
10 #SBATCH --error=slurm-%j.err
11 #SBATCH --mail-type=ALL
12 #SBATCH --mail-user=sanga@itu.edu.tr
13
14
15 export OMP_NUM_THREADS=1
16
17 echo "SLURM_NODELIST $SLURM_NODELIST"

```

```

18 echo "NUMBER OF CORES $SLURM_NTASKS"
19
20 module purge
21 module load centos7.3/comp/intel/PS2018-update2
22
23 ESPRESSO_DIR=/truba/home/csanga/espresso/q-e-qe-7.0/bin
24
25 mpirun -np 56 $ESPRESSO_DIR/pw.x -npool 56 <0.00575-scf←
    .in> 0.00575-scf.out
26 mpirun -np 56 $ESPRESSO_DIR/ph.x <0.00575-ph.in> ←
    0.00575-ph.out
27 mpirun -np 56 $ESPRESSO_DIR/q2r.x <0.00575-q2r.in> ←
    0.00575-q2r.out
28 mpirun -np 56 $ESPRESSO_DIR/matdyn.x <0.00575-matdyn.in←
    > 0.00575-matdyn.out
29 mpirun -np 56 $ESPRESSO_DIR/plotband.x <plotband.in> ←
    plotband.out
30 eval "$(/truba/home/csanga/miniconda3/bin/conda shell.←
    bash hook)"
31 python3.9 ph_plot.py
32
33 mpirun -np 56 $ESPRESSO_DIR/pw.x -npool 56 <0.00575-←
    nscf.in> 0.00575-nscf.out
34 mpirun -np 56 $ESPRESSO_DIR/epw.x -npool 56 <epw.in> ←
    epw.out
35
36 outfolder=results_GMKG_1001
37 mkdir $outfolder
38
39
40 mpirun -np 56 $ESPRESSO_DIR/epw.x -npool 56 <0←
    _complex_GMKG_1001.in> ./ $outfolder/gkk.out
41
42 #Postprocess results
43 mkdir ./ $outfolder/enk
44 mkdir ./ $outfolder/enkq
45 mkdir ./ $outfolder/omega
46 mkdir ./ $outfolder/gkk_abs
47
48 for i in 7; do
49 for j in 7; do
50 for k in 1 2 3 4 5 6 7 8 9; do
51 grep "${i}          ${j}          ${k}" ./ $outfolder/gkk.←
    out | awk '{print $4}' > ./ $outfolder/enk/enk_${k}.←
    dat
52 grep "${i}          ${j}          ${k}" ./ $outfolder/gkk.←
    out | awk '{print $5}' > ./ $outfolder/enkq/enkq_${k}←
    }.dat

```

```
53 grep "${i}          ${j}          ${k}" ./$outfolder/gkk.↵  
    out | awk '{print $6}' > ./$outfolder/omega/omega_${↵  
    k}.dat  
54 grep "${i}          ${j}          ${k}" ./$outfolder/gkk.↵  
    out | awk '{print $7}' > ./$outfolder/gkk_abs/gkk_${↵  
    k}.dat  
55 echo "${k} is done"  
56 done  
57 done  
58 done  
59  
60  
61 exit
```



APPENDIX B - DERIVATION FOR KOHN-SHAM EQUATIONS

According to the Hohenberg-Kohn theorem, the total energy E of the system is a functional of the electronic charge density $n(\mathbf{r})$, and can be stated mathematically as $E = F[n(\mathbf{r})]$. The functional and hence E , can be written as [17];

$$F[n] = \int d\mathbf{r} n(\mathbf{r})V_n(\mathbf{r}) - \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \psi_i(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \quad (\text{A.1})$$

First three terms on the right describe total energy of the system under independent electron approximation. First term is the interaction with the external potential $V_n(\mathbf{r})$, second term is the kinetic energies of the "independent" electrons where ψ_i is the electron wave function and index i runs over all electron wave-functions from 1 to total number of N . Third term is the Hartree energy. The final term E_{xc} stems from the approximation errors of making the independent electron approximation and has to be determined to further analyze the system. The electron density of the system can be expressed in terms of Kohn-Sham wavefunctions ψ_i , the system is still unsolved and wave-functions are unknown, but the relation between them and the electron density is still true.

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (\text{A.2})$$

We also need some functional derivative relations to derive the equations. According the HK theorems, the minimum of the total system energy is accompanied by the ground state electron density. This is stated as;

$$\frac{\delta F}{\delta n} = 0 \quad (\text{A.3})$$

Using eq. A.3 and eq. A.2, we can evaluate the expression;

$$\frac{\delta F}{\delta \psi_i^*} = \frac{\delta F}{\delta n} \frac{\delta n}{\delta \psi_i^*} = \frac{\delta F}{\delta n} \psi_i = 0 \quad (\text{A.4})$$

Functional derivative must satisfy the property; [59];

$$\int d\mathbf{r} h(\mathbf{r}) \frac{\delta F}{\delta g}(\mathbf{r}) = \left. \frac{d}{d\varepsilon} f[g(\mathbf{r}) + \varepsilon h(\mathbf{r})] \right|_{\varepsilon=0} \quad (\text{A.5})$$

Using this relation we can take the derivative of eq. A.1 and get;

$$\frac{\delta F[n]}{\delta \psi_i^*} = V_n(\mathbf{r}) - \frac{\nabla^2}{2} + \int d\mathbf{r} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}}{\delta n} \quad (\text{A.6})$$

Adding the Kohn-Sham wave-functions;

$$\left[-\frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (\text{A.7})$$



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2024