Calculation of phonon dispersion relation using new correlation functional

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Abstract. To extend the use of Local Density Approximation (LDA), a new analytical correlation functional is introduced. Correlation energy is an essential ingredient within density functional theory and used to determine ground state energy and other properties including phonon dispersion relation. Except for high and low density limit, the general expression of correlation energy is unknown. The approximation approach is therefore required. The accuracy of the modelling system depends on the quality of correlation energy approximation. Typical correlation functionals used in LDA such as Vosko-Wilk-Nusair (VWN) and Perdew-Wang (PW) were obtained from parameterizing the near-exact quantum Monte Carlo data of Ceperley and Alder. These functionals are presented in complex form and inconvenient to implement. Alternatively, the latest published formula of Chachiyo correlation functional provides a comparable result for those much more complicated functionals. In addition, it provides more predictive power based on the first principle approach, not fitting functionals. Nevertheless, the performance of Chachiyo formula for calculating phonon dispersion relation (a key to the thermal properties of materials) has not been tested yet. Here, the implementation of new correlation functional to calculate phonon dispersion relation is initiated. The accuracy and its validity will be explored.

1. Introduction
In recent decades, major technology has been transformed into a very small scale, thanks to the large investment in silicon nanofabrication techniques. This trend makes great revolutions in our society. In the applications of thermoelectric devices, we seek for the materials that can conduct electricity easily, but block the motion of heat. In converse, finding better ways to dissipate heat is a key requirement as the devices become smaller and chips get faster. It is important to control heat transfer in these crystalline materials. Unlike bulk material, there are many evidences indicate the violation of Fourier’s law in low dimensional lattices [1]. The aim to control heat transport grounds on the understanding of phonon behaviour.

Phonon is the physical particle representing mechanical vibration [2-3]. Above the absolute temperature, even in solid, the atoms are never in the static state. They always oscillate around their equilibrium points. Because atoms are arranged very tightly, all atoms stay very close to their neighbours and are connected to each other by chemical bonds. This can be compared to the spring-mass system, where atoms represent the mass and their chemical bonds represent the spring. When the
material is heated, atoms start moving and travel far from their equilibrium points. The atom will exert a force on the neighbour atoms and push them to move. This results in the creation of “phonon”, a lattice vibration wave, which is the major heat carrier and responsible for the heat transmission through the semiconductor. On the other hand, the oscillation of phonons with different frequencies can be seen as the special wave of lattice distortion that propagates through the solid. A wave has a fixed relationship between two points in space or at two different times. The wave characteristics of phonons are important for transport processes in nanostructures, where waves will experience the phenomena of reflection and refraction.

In quantum mechanics, Schrödinger equation is generally used to describe the quantum state in terms of wave functions. Phonon dispersion relation (relationship between frequencies and wave vectors) is calculated using ground-state energy obtained from Kohn-Sham equation. This approach takes an advantage of mapping a complex many electrons interaction system to an equivalent non-interaction electron system. Once the phonon dispersion is known, the essential thermal properties such as heat capacity and thermal conductivity can be further calculated. Unfortunately, the correlation energy (a crucial ingredient of Kohn-Sham equation) is an unknown term and we do not have the analytical expression for it. The quality of the correlation energy approximation will have an effect on the accuracy of the modelling system. There are many fitting correlation functionals obtained from parameterizing Ceperley-Alder near exact Monte-Carlo work such as Vosko-Wilk-Nusair, VWN (1980) and Perdew-Wang, PW92 (1992) [4-6]. Nevertheless, these functionals are in a very complex fitting-parameters form (not analytical).

Chachiyo correlation functional is introduced as a latest analytical correlation functional in a very simple form but still provides accurate results compared with the previous approaches. This correlation functional will expand the new area of phonon calculation and encourage more predictive simulation power.

2. Theory

2.1. Density functional theory

Density functional theory (DFT) is the computational technique used in quantum mechanical modelling to determine the ground state electronic structure of the system. According to the theory, properties of the system can be determined using the functional, function of another function. In this case, the energy of the system is in the functional form of the electron charge density $n(r)$.

$$E[n(r)] = F[n(r)] + \int n(r) V(r) \, dr$$

(1)

where $F[n(r)]$ and $V(r)$ are the universal functional and the external potential respectively.

The electron charge density that minimizes equation (1) coincides with the ground-state energy. The challenge is that the form of the universal function $F[n(r)]$ is not known. Kohn and Sham [7] equation is the useful technique for dealing with this problem by mapping the problem of interacting electrons onto the auxiliary system of non-interaction electrons with an appropriate approximation.

2.1.1. Kohn and Sham equation.

In general, if the strength of electron-electron interaction disappears, the universal functional $F[n(r)]$ is the ground-state kinetic energy, as a function of its electron charge density, of the non-interaction electron system. Using Kohn-Sham approach, the ground-state energy in equation (1) is expressed in the following terms:

$$\left\{-\frac{1}{2} \mathbf{r}^2 + V_{\text{nic}}(r) + V_H[n(r)] + V_{xc}[n(r)] \right\}\psi_i(r) = \epsilon_i \psi_i(r)$$

(2)

where the first three terms are kinetic energy, electron-nucleus interaction and Hartree potential of electron charge density. $V_{xc}[n(r)] = \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$ is exchange-correlation potential and $E_{xc}[n(r)]$ is exchange-correlation energy.

2.1.2. Local-density approximation.
Compared to the total energy, exchange-correlation energy may occupy a little portion but leads to the quality of calculation. This energy is unfortunately the part of energy of the system that does not have the exact expression. The more precise one can do the approximation for this energy, the more accurate the modelling system is. A general and very basic approach used to do this approximation is Local-Density Approximation (LDA) theorem. It assumes that the exchange-correlation energy of the system is similar to the exchange-correlation energy of an equal volume of the homogeneous electron gas (HEG) with the same electron charge density. Using this assumption, the exchange-correlation energy is given as the following:

\[ E_{xc}[n(r)] = \int n(r) [\varepsilon_x[n(r)] + \varepsilon_c[n(r)]] dr \]  

(3)

where \( \varepsilon_x[n(r)] \) and \( \varepsilon_c[n(r)] \) are exchange and correlation energy per particle respectively.

LDA is exact when the electron density is uniform or slowly varies. For the system that the electron density changes rapidly, this technique may give a rough approximation. Although LDA is said to be the simplest approach to do the exchange-correlation energy approximation, it works very well and provides good results in many situations beyond its limit.

### 2.1.3. Exchange-correlation energy

Exchange energy, \( \varepsilon_x[n(r)] \), is the energy reduction of the Coulomb energy caused by the antisymmetric wave functions due to Pauli exclusion principle. The exchange-energy density of HEG is known analytically [8].

Correlation energy, \( \varepsilon_c[n(r)] \), is the difference between the actual energy of a particular energy level of an atom and the calculated energy by the Hartree-Fock approximation. Except for high and low density limits, there is no exact expression form of correlation energy. Therefore the parameterization functional forms that fit to the near-exact Quantum Monte Carlo results of Ceperley and Alder such as VWN and PW are usually implemented.

### 2.2. Phonon dispersion relation

After doing various approximations, we can obtain the total energy. In addition, phonon frequencies corresponding to their wave vectors in different directions can be further calculated using dynamics matrix equation (4). Phonon dispersion relation is therefore ready to plot.

\[
\det \frac{\partial^2 \varepsilon_{st}(\mathbf{q})}{\partial^2 \mathbf{q}} = 0
\]  

(4)

where \( \varepsilon_{st}(\mathbf{q}) = \frac{1}{N_e \hbar^2 \omega_{st}(\mathbf{q})} \frac{\partial^2 E}{\partial q_s \partial q_t} \) are the inter-atomic force constants (IFCs) in reciprocal space.

### 3. Method

The typical correlation functionals are in a complex form and difficult to implement. As the latest approximation form, the Chachiyo correlation functional [9] is introduced in a very simple form. Different from VWN and PW correlation functionals that aim to fit with the near exact Monte Carlo data, Chachiyo correlation functional is derived independently from the second-order Møller-Plesset perturbation theory (MP2) [10] as shown below.

\[ \varepsilon_c(r_s) = a \ln(1 + \frac{b}{r_s} + \frac{b}{r_s^2}) \]  

(5)

where \( r_s = \left( \frac{4\pi \rho}{3} \right)^{-1/3} \) is the Wigner-Seitz density parameter, \( \rho \) is the electron density, \( a \) and \( b \) are known constants from high density limit.

Interestingly, this formula provides an accurate approximation of correlation energy compared to the Monte Carlo result and the complex VWN fitting form. Chachiyo correlation functional is therefore initiated here to implement in equation (3) and further calculate phonon dispersion relation. All phonon calculation is obtained from QUANTUM ESPRESSO package, which is widely used in the nanoscale simulation research area. Unfortunately, there is no open source code of pseudopotential generation that implements Chachiyo correlation functional yet because it is a new correlation functional. Chachiyo formula has to be manually inserted into LibXC [11], which is the database used...
in the calculation. Pseudopotential and phonon dispersion relation are then generated by APE (atomic pseudopotentials engine) and QUANTUM ESPRESSO package respectively [12-13].

4. Expected result
Good convergence and transferability of pseudopotential obtained from Chachiyo formula is anticipated. The validity of this new analytical correlation functional to extend the use of local density approximation within phonon calculation from fitting to first principle approach will be explored. It is expected to provide a good agreement with experimental data and a comparable modelling result with the typical functionals. Frist principle method will encourage more prediction power in the modelling system. The simplicity of this formula is hoped to reduce the calculation time for complex crystal.

5. Conclusion and future plan
Chachiyo correlation functional is initiated to implement the calculation of phonon dispersion relation. The key advantages of this formula are the first principle approach and the simplicity form. The phonon dispersion relation obtained can be used to further calculate and investigate important thermal properties such as heat capacity and thermal conductivity. Alternatively, besides phonon calculation, Chachiyo formula is also applicable to the calculation of electronic band structure and density of states of materials in future work.

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