

Inclusion of second derivatives in the expansion of the electron-lattice interaction from second principles

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December 2023

Abstract

From a theoretical point of view, a monoatomic chain formed by hydrogens has been studied in order to determine the parameters that characterise it with first principles techniques using SIESTA, in order to study the characteristics of the Peierls distortion, metal-insulator transition; and to control its emergence and properties at will by modifying the system with external potentials and different models for the dependence between the hopping terms of the hamiltonian and the applied distortion.

1 Introduction and motivations

One of the most general ways of classifying solid systems is by their electronic characteristics, namely whether or not they conduct electric current. From this point of view, it is possible to distinguish, loosely, between conducting, semi-conducting and insulating systems (although there is a spectrum between the latter two). There are all kinds of solid systems that allow transitions between these states, which can be studied from the point of view of electron-lattice interactions, as is the case, for example, of the Peierls transition. In this project, the characteristics of this phenomenon have been studied from a theoretical point of view, for the subsequent determination of the relevant parameters using first-principles techniques with SIESTA.

The Peierls transition is the dimerisation of a system that occurs when the net energy of the system decreases as it is distorted, due to an increase in its electronic stability, although some mechanical energy is required to disrupt it and separate the atoms from their equilibrium positions.

These kinds of transitions are really important and can have all kinds of applications. Basically, an insulating system and a conducting/semiconducting system have extremely different characteristics, so the fact that transitions between these states exist and can be controlled at will by means of external fields is extremely powerful.

2 Working framework

In order to analyse the electron-lattice interaction within a solid, it is necessary, first of all, to obtain from a theoretical point of view the electron and phonon energy distributions. With the appropriate theoretical expressions, it is possible to approach the problem from a computational point of view, finding the necessary quantities from first principles.

To obtain the electronic energy, use will be made of the band model, for the determination of which the tight binding model will be used. This model is based on one main

assumption: the potential of the complete solid in the environment of a nucleus is, essentially, that of the nucleus in question. This premise motivates the following approach: the wave functions of the whole solid will be considered to be linear combinations of the wave functions of its constituent atoms, the LCAO (Linear Combination of Atomic Orbitals) approach.

The secular equation which allows the determination of the electronic band structure of a system, $E(\vec{k})$, where \vec{k} are the wave vectors of the reciprocal space; deduced from the premises of this model, is the following:

$$|H(\vec{k}) - E_n(\vec{k})S(\vec{k})| = 0 \quad (1)$$

where $H(\vec{k})$ and $S(\vec{k})$ are the hamiltonian and overlap matrices, respectively, both in reciprocal space, which are defined as the discrete Fourier transform of these matrices in real space:

$$H(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\vec{T}} \langle \chi_{\nu\vec{T}} | \hat{h} | \chi_{\mu\vec{T}} \rangle \quad S(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\vec{T}} \langle \chi_{\nu\vec{T}} | \chi_{\mu\vec{T}} \rangle$$

where \vec{T} is any translation vector in real space, χ is an atomic orbital, and the subscripts ν and μ run through the different orbitals present in the solid.

The key to solving this equation in a relatively simple way and, thus, obtaining the band structure that describes the system to some extent is to select the approximations in a coherent way.

On the other hand, as for the interactions of the lattice per se, the vibrations present in the lattice; the phonon model will be used, which is based on bosonic pseudoparticles that describe the normal modes of vibration of the system. Using this model, it is possible to arrive at the following equation, known as the dynamic equation, the solution of which gives rise to the modes of vibration of the system:

$$\tilde{D}(\vec{q})\gamma(\vec{q}) = \omega^2(\vec{q})\gamma(\vec{q}) \quad (2)$$

where \vec{q} are the wave vectors of the vibrations, $\gamma(\vec{q})$ are the phononic eigenvectors and $\omega(\vec{q})$ are the phononic frequencies.

The dynamic matrix is the one that contains, as its name indicates, the information about the dynamics of the lattice points as they move around their equilibrium point. This matrix is closely related to the force constant matrix, the diagonalisation of which characterises the vibrations, which are fundamental to finding the vibrational energies of the system.

2.1 First principles techniques

In the context of Condensed Matter Physics, first-principles simulations are a set of computational techniques that allow, in the absence of any experimental results beyond the fundamental constants of nature, to solve the Schrödinger equation.

There are different ways of approaching these problems, resulting in a number of different techniques. On the one hand, there are the Hartree-Fock techniques, which focus on the study of the overall wave function of the system, composed of Slater determinants of one-electron wave functions. For this, average potentials are studied, assuming that each individual electron is subjected to these fields. The fundamental problem with this method is that it is computationally demanding, so it is not very suitable for large systems.

In order to deal with much more complex systems from first principles, the Density Functional Theory (DFT), which has a significantly different approach, is often used. The fundamental difference is that this theory does not work with the wave function of the system as a whole, but with the density functional, which, in intuitive terms, associates the electron density at different points in space with different observables of the system, such as the energy. The goal of this theory is to find that functional (and, therefore, that electronic distribution) which minimises the energy of the system, for which there are a series of theorems proved by Kohn, which earned him the Nobel Prize in 1998. In addition to this functional, others such as the correlation functional are often used to describe electron-electron interactions, which avoids the fundamental Hartree-Fock problem, the need to consider each electron individually. These theories provide results with high accuracy, considering the low computational cost compared to Hartree-Fock.

2.1.1 SIESTA

In the context of this research we will make use of SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms, [1]), which is a first-principles computational method and software that allows all kinds of calculations to be carried out on the electronic dynamics of a large system. One of its most relevant features is the fact that it is based on the method of the self-consistent Kohn-Sham density functional, making use of approximations for

the correlation-exchange functional such as the local density approximation or the generalised gradient approximation, among many other possibilities. SIESTA offers the possibility to determine a large amount of information about a system, such as the electron density itself, band structure, interatomic forces, energy, phonons, calculation in variable cells, and so on. All relevant information about the specific operation can be found on the official website in the documentation section [2], and in more detail in [3].

3 Peierls transition for a monoatomic hydrogen chain

First of all, a theoretical analysis of the problem will be carried out, and then it will be approached with first principles techniques.

Suppose a one-dimensional monoatomic solid consisting of hydrogen atoms with lattice parameter a . Using the tight binding model to determine the dispersion relation, i.e., the band structure of the solid, it is obtained that it has a cosine shape.

Now, a priori, there is nothing to ensure that the system is not truly in a metastable state, and that as a result of some kind of perturbation in it, a lower energy state could be reached. When the system is undistorted, i.e. with the nuclei in their equilibrium position, its energy is mainly due to the electronic energy. However, there is the possibility that by distorting it, from the electronic point of view the system increases its stability; but from the mechanical or vibrational point of view it does not, because by displacing the nuclei from their equilibrium position a positive contribution to the total energy, an elastic energy, appears. Stability in a distorted system would be achieved if the net energy, despite the positive contribution, is lower than the undistorted energy.

Consider that the motion of the atoms in the lattice is, for simplicity, contained in the axis aligned with the lattice points. These distortions will be given by phonons, such that the motion of a given lattice point will be:

$$Q(\vec{r} - \vec{R}) = Q_0 e^{i\vec{k}\vec{R}} \quad (3)$$

where \vec{k} is the position of the phonon in the reciprocal space.

Although there are several possibilities, there are two particularly simple lattice distortions: first, that the phonon is at the zone center, which corresponds to a translation, and therefore, leaves the system completely invariant.

On the other hand, it is possible to consider a distortion caused by a phonon at the zone edge:

$$Q(\vec{r} - \vec{R}) = Q_0 \exp(i\frac{\pi}{2a}m2a) \quad \text{where } m \in \mathbb{Z}$$

Which would result in a deformation of the form:

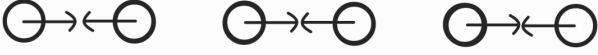


Figure 1: Distortion caused by a phonon at the zone edge.

that is, essentially, the dimerization of the system.

To study the effects of this disturbance, using the following approximations, we will solve the secular equation (1):

1. Localised orbitals: considering that the atomic orbitals nullify for relatively small distances, the matrix elements $H_{\mu\nu}$ will be neglected for long distances.
2. The energy of an orbital, $H_{\mu\mu} = \alpha$, is simply that of the atom in the absence of the rest of the system. This is reasonable given one of the assumptions of the tight binding model: the potential felt by an electron in the environment of a nucleus is essentially that generated by the nucleus. Moreover, for simplicity, given that the origin of energies can be taken wherever one prefers, it will be considered as $\alpha = 0$.
3. Given the geometry of the system, two hopping terms should be considered, and treated as distinct. One of them for nearby atoms, $H_{\mu\nu}(\vec{0}) = \Gamma$, and another for distant adjacent atoms, $H_{\mu\nu}(\vec{T} = 2a) = \gamma$, such that: $|\Gamma| > |\gamma|$. This is coherent since it is expected that the facility for electrons to "hop" between two close nuclei is higher than when they are distant. In addition, the first-neighbour approximation will be considered.
4. Lastly, the orbitals are to be considered orthogonal between themselves, that is, they overlap only with themselves.

Using the equation (1) and taking these approximations into account, it is possible to obtain, after a series of simplifications:

$$E_n = \pm \sqrt{(\Gamma - \gamma)^2 + 4\Gamma\gamma \cos^2(ka)}$$

The graphical representation of these energy bands, taking $a = 1\text{\AA}$ and different values for Γ and γ , is shown in Figure 2, where it can be seen that for $\Gamma = \gamma$ the problem reduces to a non-dimerised chain with two orbitals per unit cell. However, as the difference between Γ and γ increases, the degeneracy at the zone edge disappears and an energy gap opens up, which increases as the distance between dimers increases, observing, indeed, a metal-insulator transition.

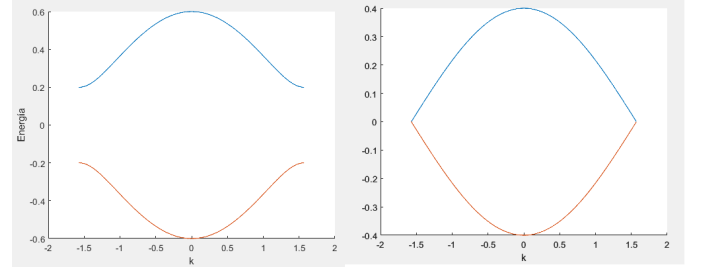


Figure 2: Graphical representation of the energy bands for dimerised hydrogen. On the left, with hoppings $\Gamma = -0.4$ eV and $\gamma = -0.2$ eV. On the right, with $\Gamma = \gamma = 0.2$ eV.

Once the electronic bands have been obtained, it is easy to compute the difference in electronic energy between the dimerised and non-dimerised systems, since it is sufficient to integrate the difference between the dispersion relationships in each case. After a series of variable changes to obtain an elliptic integral of the second kind, it is possible to approximate this energy as (see [8]):

$$\Delta E_{elec} \approx -\frac{4}{\pi} \left(2\beta + \sqrt{(\Gamma - \gamma)^2 + 4\Gamma\gamma} \left[1 + 0,463\lambda - \frac{\lambda}{4} \ln(\lambda) \right] \right)$$

where λ is a characteristic parameter of the elliptic equations, depending in this case on the hopping terms, and β is the energy of the atomic orbitals in the non-dimerised system.

On the other hand, to obtain the difference in vibrational energies, which is essentially the elastic energy of the distorted system, it is possible to make use of the phonon model. The relation $\omega - k$ for a monoatomic chain can be derived in a simple way (it is given below), such that, specifying for a phonon at the zone edge and taking the expression for the elastic energy, one obtains:

$$E_{phon}^{elast} = 4CQ^2$$

where C is the elastic constant and Q is the displacement of the nuclei from their equilibrium position.

The elastic constant for a monoatomic chain can be easily obtained by taking into account the dispersion relation $\omega(k)$:

$$\omega^2 = 2 \frac{C}{M} \cdot (1 - \cos(ka))$$

where M is the mass of the nuclei. In the vicinity of the Γ point, where $k \approx 0$, which corresponds to long frequencies, it is possible to approximate:

$$1 - \cos(ka) \approx \frac{1}{2}(ka)^2$$

Which, substituting in the dispersion relation and deriving with respect to k , it can be deduced that:

$$C = \frac{M}{a^2} \left(\frac{d\omega}{dk} \right)^2$$

So, once the phononic bands are known, it is possible to derive around the Γ point and find C .

Once the relevant equations have been determined from a theoretical point of view, it is possible to tackle the problem with first-principles techniques. The main objective is to determine the different parameters that govern the Peierls transition: the elastic constant, the hopping terms and the energy of the involved atomic orbitals.

4 Computing with SIESTA

4.1 Relaxation of the lattice

First, SIESTA will be used to find the interatomic distances for the hydrogen chain. To do this, a solid is created consisting of hydrogen atoms aligned along the z-axis, separated by an arbitrary distance, and SIESTA is used to relax the lattice. This procedure consists of considering different interatomic distances, and computing in each case the force between the atoms, until it is small enough to be considered zero, and to achieve self-consistency. For this process, the conjugate gradient method is selected. With this relaxation, a value of the lattice parameter $a \approx 2.1187$ Bohr has been obtained.

4.2 Determination of electronic bands

Once the relaxed lattice has been determined, it is possible to compute the band structure. To do this, SIESTA is executed by providing the previously obtained lattice, making use of the LDA (Local Density Approximation) functional. With this, SIESTA computes, among other information, the values of the electronic energy of the system for different wave vectors.

4.3 Determination of phononic bands

This process is more complex and requires a greater number of intermediate steps.

4.3.1 Definition of the supercell

A supercell is created, which takes the role of the unit cell; that consists of an extended cell, made up of several unit cells. One has to make sure that the unit cell is large enough so that all atoms that suffer non-negligible distortion effects at a specific point are considered. In this case, a supercell consisting of five hydrogen atoms, the central one, two on the right and two on the left, will be considered. They will all move a distance of 0.04 Bohr, in the three directions of space.

4.3.2 Force constants matrix

Once the supercell has been created, it is proceeded with the displacement of the different atoms. SIESTA is used

to determine the interatomic forces that arise between the atoms when they are displaced along the three directions of space, carrying out a loop for every direction and for every atom in the supercell, thus obtaining the force constants. This whole process is carried out using the finite differences method.

4.3.3 Dynamic matrix

Once the force constant matrix has been obtained, it is possible to find the dynamic matrix by carrying out the discrete Fourier transform, which allows us to solve the equation (2) and thus obtain the angular frequencies of the vibration modes as a function of the wave vector in the reciprocal space, i.e. the phononic bands.

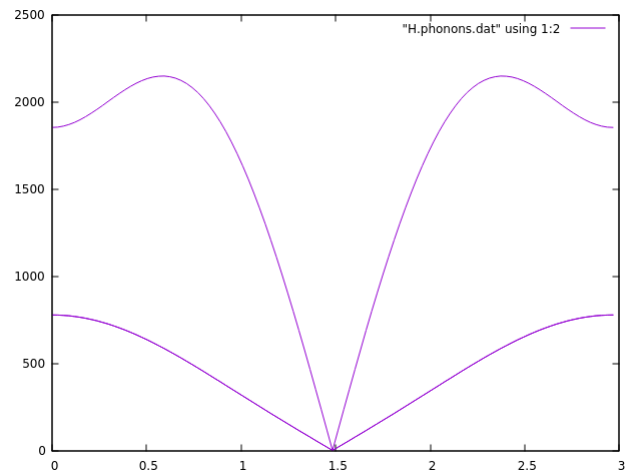


Figure 3: Graphical representation of the phononic bands obtained with SIESTA, angular frequencies on the vertical axis and wave vectors on the horizontal axis.

By computing the derivative of ω as a function of k around the point Γ , as mentioned above, it is possible to determine, finally and from first principles, the elastic constant characterising the vibrations in the solid. Knowing this magnitude and the total electronic energy of the system, it is possible to check whether the dimerised system has a higher or lower stability than the non-dimerised system.

It is possible to recreate the Peierls transition and control its appearance and qualities, for which it is necessary to simulate how the Tight Binding parameters change, in this case the two hopping terms and the energy of the orbitals involved. There is also the possibility of subjecting the system to external potentials which, in essence, modify the interatomic interactions and force the system to change.

A really simple example to illustrate these ideas and allows to observe this transition is to consider a linear relationship between the hopping terms and the distortion of the system, which can be achieved by a first order Taylor expansion:

$$\Gamma = \gamma_0 + f \cdot Q$$

$$\gamma = \gamma_0 - f \cdot Q$$

where f is simply a proportionality constant.

With this proposition and the analytic equations previously exposed, one can obtain the following relationship in the energy difference between the dimerised and undimerised systems:

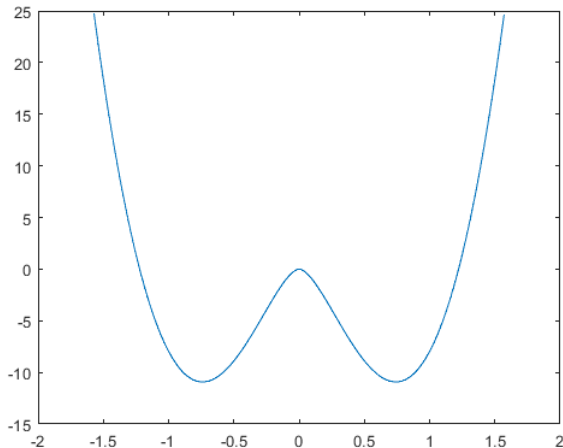


Figure 4: Graphical representation of the difference in energies of the undistorted system and the dimerised one (vertical axis), as a function of the displacement of the atoms from their equilibrium position (horizontal axis). Arbitrary parameters have been considered, with units of no relevance: $a = 1$, $\gamma_0 = -0.4$, $f = 0.5$, $C = 0.1$.

Where it can be clearly seen that the non-dimerised system is, in fact, a metastable state (for the given parameters), and two potential wells appear (symmetrical with respect to $Q = 0$ due to the symmetry of the solid with which we are working). Under these circumstances, the system would dimerise automatically under any perturbation, which is not necessarily the general case. The characteristics of this phenomena will depend on the values of the parameters and their dependencies on the distortion and the other characteristic quantities of the system, which can be fully explored using SIESTA.

5 Conclusions

The phenomenon of Peierls distortion, which involves a metal-insulator transition for a given solid system, can be studied using first-principles techniques, providing all kinds of information about its characteristics and the different cases to which it gives rise. It is possible to modify the conditions to which the system is subjected, as well as the model that describes the variation of the Tight Binding parameters with the applied distortion, using SIESTA, observing cases such as that the non-dimerised system is nothing more than a state in unstable equilibrium, which under any minimum perturbation will automatically be distorted

by the variation in the electronic energy resulting from the structural modifications, increasing the stability to such an extent that it is capable of compensating the loss of elastic energy.

First-principles techniques are very powerful in theoretical physics, enabling one to reach regions of physics that would be absolutely impossible without the use of computation. Moreover, it is an ever-expanding area, and advances in this area are leading to ever higher precision calculations.

6 Acknowledgements

Thanks are due to the División de Física de la Materia Condensada for the opportunity to develop this project, condensed and very summarised in these pages. Specifically, to my tutor Francisco Javier Junquera Quintana, for guiding me through the whole process and for sharing his interest and passion with me in this field of Physics and Computing.

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