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Bachelorthesis

Optimization of the Quantum Espresso Density Functional Theory Code for parallel execution on the PHYSnet-Cluster

vorgelegt von

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Todo list

Kurzzusammenfassung

Diese Arbeit untersucht Quantum ESPRESSO, eine Sammlung von Programmen für Berechnungen von elektronischen Strukturen und Modellierung von Materialien in Bezug auf seine Skalierbarkeit über mehrere Prozessoren auf dem PHYSnet compute cluster. Die Methode ist eine Reihe an Benchmarks zum Testen von verschiedenen Compiler Kombinationen und den Parallelisierungsoptionen von Quantum ESPRESSO. Diese Benchmarks zeigen, dass die Nutzung von Compilern in Intel oneAPI die Skalierbarkeit signifikant verbessert und dass außerdem die Nutzung der Parallelisierungsoptionen von Quantum ESPRESSO die Rechnungen weit über einen Rechnerknoten hinweg ermöglichen, wenn sie richtig genutzt werden. Ergebnisse aus den Benchmarks wurden außerdem genutzt, um effiziente Phononen Rechnungen von TaS_2 in einer Ladungsdichtewellephase duchzuführen, deren Ergebnisse möglicherweise eine Lücke um das Fermi-Niveau zu erklären, die 2019 in einem Scanning Tunneling Spectroscopy (STS) Experiment an diesem Material gefunden wurde.

Abstract

This thesis examines Quantum ESPRESSO, a suite of computer code for electronic-structure calculations and materials modeling in terms of its scalability on multiple processors on the PHYSnet compute cluster. A series of benchmarks is carried out to test different combination of compilers as well as parallelization parameters offered by Quantum ESPRESSO itself. These benchmarks show that using a set of compilers and auxiliary code in Intel oneAPI significantly improves scaling and that the parallelization parameters offered by Quantum ESPRESSO let calculations scale beyond a single node when used right. Results from these benchmarks were then used to carry out efficient phonon calculations on TaS_2 in a charge density wave phase, the results of which could possibly explain a gap feature near the Fermi niveau observed in a 2019 STS experiment on this material.

Contents

Motivation

For a realistic description of matter, description derived from first principle (so called ab-initio methods) are needed. Phenomenons explainable only from ab-initio methods range from the thermodynamic properties of matter which are directly tied to phonons, i.e. quasi particles emerging in the quantization of vibrational modes, to phenomenons like superconductivity, which still don't have established theories explaining every kind of superconductor.

One such ab-initio method is Density Functional Theory (DFT), the foundations of which were laid in 1964 by Hohenberg and Kohn [1] and in 1965 by Kohn and Sham [2]. Since 1990, methods within the density functional formalism have been very successful across a number of disciplines in physics, chemistry and biology, with over 160000 publications on the topic between 1990 and 2015 [3]. The appeal of DFT methods lies in the fact that the complexity of calculations is reduced in such a way that while properties such as the full wave function cannot be computed, total energies are very reliably produced, which in turn enables calculations of lattice dynamics, thermodynamical properties of matter or chemical reactions. These calculations are computationally cheap in comparison to methods working with full wave functions, so that simple systems can be simulated on a home computer today. In software suites such as Quantum ESPRESSO [4, 5], DFT methods are easily available today.

Going beyond simple calculations of a few atoms and towards current research questions makes parallel calculations over multiple nodes on compute cluster with hundreds or thousands of CPUs the only feasible possibility. An important step is as such making sure the process of scaling the work across multiple processors is done in an effective manner to utilize available computing resources as efficient as possible.

Thus, the task of this thesis was two-fold: First, examining the way Quantum ESPRESSO calculations are best parallelized on the PHYSnet cluster and then using this knowledge to run calculations for a system of current interest and possibly explain recent experimental data of this system [6].

The examined system is TaS_2, a Transition Metal Dichalcogenide (TMDC). Recent discovery of freestanding monolayers of TMDCs [7] has brought these materials into focus. TaS_2 in particular is notable

a little bit more about TaS2, why its interesting

The structure of this thesis is as follows: first, all relevant theory needed to understand the calculations made with Quantum ESPRESSO will be outlined in ch. I. Following that, details regarding the computational work done, such as the concrete metrics evaluating performance as well as a description of the parallelization parameters offered by Quantum ESPRESSO will be presented in ch. II. Ch. III examines scalability of the `PWscf` module, which enables electronic structure calculations, the same is done in ch. IV for the `PHonon` module, which is used for calculation of phonon and phonon related properties. The results from these chapters are then used to run an optimized phonon calculation on TaS_2 in the charge density wave

phase. This optimized phonon calculation is then the foundation for a possible explanation of experimental data on TaS_2 in ch. V.

Conventions

Throughout the text of this thesis scalars are written in italic s, vectors in bold italic $\boldsymbol{v}$ and matrices in bold $\mathbf{M}$ fonts. The summation/multiplication over nearest neighbour sites i and j is $\langle ij \rangle$ as a subscript to $\sum/\prod$. Furthermore, Hartree atomic units are used in general and only in selected instances it is deviated from this: $\hbar = m_\mathrm{e} = \mathrm{e} = {}^{4\pi}/_{\varepsilon_0} = 1$.

I Ab initio methods for materials modeling

is formulated better, but still not perfect

The description of matter from theoretical methods starts from the Hamiltonian of an interacting system of electrons and nuclei (with electrons coordinates $\boldsymbol{r}_i$ and nuclei coordinates $\boldsymbol{R}_\alpha$)

$$\hat{H} = \hat{T}_\mathrm{e} + \hat{U}_\mathrm{e-e} + \hat{T}_\mathrm{n} + \hat{V}_\mathrm{n-e} + \hat{W}_\mathrm{n-n} \tag{I.1}$$

$$= -\sum_i \frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 - \sum_{i,\alpha}\frac{Z_\alpha}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\beta}\frac{Z_\alpha Z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|} \tag{I.2}$$

where

- $\hat{T}_\mathrm{e}\,, \hat{T}_\mathrm{n}$ are the kinetic energies of the electrons and nuclei respectively
- $\hat{U}_\mathrm{e-e}$ is the Coulomb interaction between the electrons
- $\hat{V}_\mathrm{n-e}$ is the Coulomb interaction between the electrons and the nuclei
- $\hat{W}_\mathrm{n-n}$ is the Coulomb interaction between the nuclei.

This very general problem consisting of both the electronic and nuclei degrees of freedom can be simplified in a first step by employing the Born-Oppenheimer approximation [8]. The approximation assumes the nuclei to be fixed point charges which create a potential for the N interacting electrons, so that the electronic part can be solved independently using the nuclei positions $\boldsymbol{R}$ as a parameter

$$\hat{H}_\mathrm{BO} = \hat{T}_\mathrm{e} + \hat{U}_\mathrm{e-e} + \hat{V}_\mathrm{n-e} + \hat{W}_\mathrm{n-n} \tag{I.3}$$

$$= -\sum_i \frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i\sum_\alpha \frac{Z_\alpha}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\beta}\frac{Z_\alpha Z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}\,. \tag{I.4}$$

The terms $\hat{V}_{n-e}$ and $\hat{W}_{n-n}$ here are just a function of the electronic coordinates $\boldsymbol{r}$ and a constant respectively, so they can then be combined into a potential $\hat{V}(\boldsymbol{r})$ for the interacting electrons, so that the Hamiltonian reads

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}\,. \tag{I.5}$$

I.1 Density Functional Theory

Obtaining solutions to the Schrödinger equation with the Hamiltonian I.4 is analytically impossible, as it produces a system of $3N$ coupled differential equations, with $N \sim N_\mathrm{Avogadro} \sim \mathcal{O}(10^{23})$. As such, the need for good approximations to obtain results for real world systems is high. One particularly successful approach is Density Functional Theory (DFT). In the

following section, the theoretical framework of DFT will be reviewed following the PhD thesis of Nicola Marzari [9], a more extensive discussion can be found in Richard Martins textbook on electronic structure [10].

I.1.1 Hohenberg-Kohn theorems

The start for DFT is the exact reformulation of the electronic structure problem by Hohenberg and Kohn [1]. This reformulation uses the ground state density of the electronic system $n_0(r)$ as the basic variable. To achieve this, Hohenberg and Kohn [1] formulated two theorems, which demonstrate that the ground state properties of an electronic system can be described using the ground state density (the proof of those theorems is omitted here, but can be found in the original publication [1] or the textbook by Martin [10, chapter 6.2]):

I The external potential is a unique functional of the ground state density.

II The ground state energy minimizes the energy functional,

$$E[n(\boldsymbol{r})] > E_0 \; \forall \; n(\boldsymbol{r}) \neq n_0(\boldsymbol{r})\,.$$

These theorems proof the existence and uniqueness of the energy functional $E[n(\boldsymbol{r})]$, but a concrete expression for it cannot be given. As the ground state wave function is a functional of the ground state density, a formal definition of the energy functional can be written as

$$\begin{aligned} E[n(\boldsymbol{r})] &= \langle\Psi|\hat{H}|\Psi\rangle \\ &= \langle\Psi|\hat{T}+\hat{U}+\hat{V}|\Psi\rangle \\ &= \langle\Psi|\hat{T}+\hat{U}|\Psi\rangle + \int \mathrm{d}\boldsymbol{r}'\, \Psi^*(\boldsymbol{r}')V(\boldsymbol{r}')\Psi(\boldsymbol{r}')\,. \end{aligned}$$

Defining the universal functional $F[n(\boldsymbol{r})] = \langle\Psi|T+U|\Psi\rangle$, which is material independent and writing $n(\boldsymbol{r}') = \Psi^*(\boldsymbol{r}')\Psi(\boldsymbol{r}')$, the energy functional becomes

$$E[n(\boldsymbol{r})] = F[n(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}'\, V(\boldsymbol{r}')n(\boldsymbol{r}')\,. \tag{I.6}$$

This is just a formal definition, as all the formerly mentioned complication of the Hamiltonian I.5 now lie in the functional $F[n(\boldsymbol{r})]$. With a known or well approximated universal functional $F[n(\boldsymbol{r})]$, the Hohenberg-Kohn theorems provide a great simplification for finding the ground state properties of a solid state system, as the problem is now only a variational problem with 3 spatial coordinates instead of $3N$ coordinates when trying to solve the full Hamiltonian.

I.1.2 Kohn-Sham equations

Kohn and Sham proposed an approach to handling interacting many-body systems by introducing an auxiliary non-interacting system of electrons [2]

$$H_0 = \sum_i^{N_e} \frac{p_i^2}{2m} + v_{\mathrm{KS}}(\boldsymbol{r}_i)\,. \tag{I.7}$$

With a correction potential v_{KS} such that the ground state charge density for the auxiliary and the interacting system are the same. This introduces a new set of orthonormal wave functions, the solutions to the non-interacting problem Ψ_i. The density for this system is calculated as

$$n(\boldsymbol{r}) = \sum_{i=1}^{N_e/2} |\Psi_i(\boldsymbol{r})|^2 \,. \tag{I.8}$$

The restriction of equality of the ground state densities for the interacting and the non-interacting system makes it possible to calculate all properties of the interacting system just by solving the non-interacting system (using the Hohenberg-Kohn theorems). This connection is shown in fig. I.1.

$$\begin{array}{ccccccc} V_{\text{ext}}(\mathbf{r}) & \overset{\text{HK}}{\Longleftarrow} & n_0(\mathbf{r}) & \overset{\text{KS}}{\Longleftrightarrow} & n_0(\mathbf{r}) & \overset{\text{HK}_0}{\Longrightarrow} & V_{\text{KS}}(\mathbf{r}) \\ \Downarrow & & \Uparrow & & \Uparrow & & \Downarrow \\ \Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) & & \psi_{i=1,N_e}(\mathbf{r}) & \Leftarrow & \psi_i(\mathbf{r}) \end{array}$$

Figure I.1: *Representation of the KS ansatz. This schema shows the connection between many-body properties on the left and the auxiliary KS system.* HK_0 *here denotes the Hohenberg-Kohn theorems applied to the auxiliary system [10, p. 137]*

The kinetic energy of such a non-interacting problem can be easily calculated as sum over all electrons

$$T_{\text{S}}[n(\boldsymbol{r})] = -\frac{1}{2} \sum_{i=1}^{N_e/2} \int \mathrm{d}^3 r \, \Psi_i^*(\boldsymbol{r}) \Delta \Psi_i(\boldsymbol{r}) \,. \tag{I.9}$$

With the help of this system and the classical electrostatic energy

$$E_{\text{H}}[n(\boldsymbol{r})] = \frac{1}{2} \int \int \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \, \frac{n(\boldsymbol{r}_1) n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{I.10}$$

an ansatz for the total energy functional in eq. I.6 can be written as

$$E[n(\boldsymbol{r})] = T_{\text{S}}[n(\boldsymbol{r})] + E_{\text{H}}[n(\boldsymbol{r})] + E_{\text{XC}}[n(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}' \, V(\boldsymbol{r}') n(\boldsymbol{r}') \,. \tag{I.11}$$

where now $E_{XC}[n(\boldsymbol{r})]$ is a functional of the density accounting for all exchange and correlation effects not present in the non-interacting electron system. The success of DFT lies in the fact that E_{XC} contributes only a small part of the total energy and can be approximated in a useful manner. Even very simple approximations to E_{XC} such as the Local Density Approximation (LDA), which uses the exchange and correlation energy of a homogenous electron gas can give accurate results for very inhomogeneous systems [11].

Using that form of $E[n(\boldsymbol{r})]$, from the variational problem (with a Lagrange parameter introduced to ensure the orthonormality of the states Ψ_i)

$$\delta \left(E[n(\boldsymbol{r})] - \sum_j \lambda_j \left[\int \mathrm{d}^3 r \, |\Psi_j|^2 - 1 \right] \right) = 0 \tag{I.12}$$

a set of single particle, Schrödinger-like equations can be derived:

$$\left(-\frac{1}{2}\Delta + \frac{1}{2}\int \mathrm{d}^3r' \, \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{\mathrm{XC}}}{\delta n(\boldsymbol{r})} + V\right)\Psi_i(\boldsymbol{r}) = \lambda_i \Psi_i(\boldsymbol{r})\,. \tag{I.13}$$

Schrödinger-like in this context means, that with the identification of the Hartree potential $V_{\mathrm{H}} = \frac{1}{2}\int \mathrm{d}^3r' \, \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$ and the exchange-correlation potential $V_{\mathrm{XC}} = \frac{\delta E_{\mathrm{XC}}}{\delta n(\boldsymbol{r})}$ the potential v_{KS} in eq. I.7 is

$$v_{\mathrm{KS}} = V_{\mathrm{H}} + V_{\mathrm{XC}} + V = \frac{1}{2}\int \mathrm{d}^3r' \, \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{\mathrm{XC}}}{\delta n(\boldsymbol{r})} + V\,. \tag{I.14}$$

Eq. I.13 become the KS equations

$$\left(-\frac{1}{2}\Delta + v_{\mathrm{KS}}\right)\Psi_i(\boldsymbol{r}) = \epsilon_i \Psi_i(\boldsymbol{r})\,. \tag{I.15}$$

Importantly, the potential v_{KS} depends on the solutions $\Psi_i(\boldsymbol{r})$, as V_{H} and V_{XC} include the density $n(\boldsymbol{r})$. The problem thus is a self-consistency problem, meaning the density used for calculating the potentials and the obtained solution only agree for the exact solution. Arriving at a solution consists then of iterating the process of obtaining a new set of potentials from the solution and solving the KS equations again.

This kind of iterative, self-consistent method lends itself to being implemented in a computational context, as every single step is mathematically simple and the complexity arises from the e.g. size of the matrices occuring or the number of steps needed, which makes calculation by hand tedious but is perfect for execution on a computer. Other methods such as the Hartree-Fock method for approximating the wave function of a many-body quantum system are also based on an iterative process.

I.1.3 Pseudopotentials and basis set

In order to represent the states and operators in eq. I.13, a basis set has to be chosen. Bloch's theorem states that in case of a periodic external potential, which makes the Hamiltonian commute with translation operators for translation by a lattice vector, the common eigenstates of these operators are:

$$\Psi(\boldsymbol{r}) = \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})\,, \tag{I.16}$$

where $\boldsymbol{k}$ is the quasi-momentum and $u_{n\boldsymbol{k}}(\boldsymbol{r})$ has the periodicity of the unit cell. A natural choice to represent $u_{n\boldsymbol{k}}(\boldsymbol{r})$ is the discrete set of plane waves $|\boldsymbol{G}\rangle$

$$\langle \boldsymbol{r}|\boldsymbol{G}\rangle = \frac{1}{\sqrt{V}} e^{i\boldsymbol{G}\boldsymbol{r}} \tag{I.17}$$

$$\implies \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} c_{n\boldsymbol{k},\boldsymbol{G}} e^{i(\boldsymbol{k}+\boldsymbol{G})\boldsymbol{r}} \tag{I.18}$$

right like that? do the plane waves have the periodicity of the unit cell?

where $\boldsymbol{G}$ is a reciprocal lattice vector. With this choice of basis set, the kinetic energy is easily calculated:

$$\langle \Psi_{n\boldsymbol{k}}(\boldsymbol{r})| - \nabla^2 |\Psi_{n\boldsymbol{k}}(\boldsymbol{r})\rangle = \sum_{\boldsymbol{G}} c^2_{n\boldsymbol{k},\boldsymbol{G}} |\boldsymbol{k}+\boldsymbol{G}|^2 \tag{I.19}$$

Another important consequence of this choice of basis set is that the electron density (eq. I.8) now becomes an integral over the Brillouin zone, which for numerical computation has to be approximated by a sum over a finite set of k points.

rete formula
nat?

One problem of this choice of basis set lies in the fact that the lower energy core electrons are very localized around the cores and as such need a lot of basis functions. Because the higher orbitals have to be orthogonal to the lower orbitals, they must also have features on the length scale of the core electrons, which means more basis functions are needed to describe them accurately.

Importantly, the core electrons don't contribute much to the electronic structure problem, so an approach to make the calculations more economically is to introduce an effective screened potential which describes the nuclear potential as well as the states close to the nucleus. These potentials are called Pseudopotentials (PP) and the orbitals constructed with them are smooth functions and can be accurately represented with a small number of basis functions. This fact can be used in computation by introducing a *cutoff energy* E_{cutoff} which limits the number of basis functions by using only expansion coefficents with $|\boldsymbol{k}+\boldsymbol{G}|^2 \leq E_{cutoff}$. Besides the number of k points, this is the second variable which can influences the computation time of DFT calculations.

should be (k+G) to the power of 2 right? also maybe concrete formula for that

With Fast Fourier Transforms FFT, an efficient algorithm exists to transform from (discrete) real to (discrete) reciprocal space. Every expectation value can be calculated in the optimal representation: in reciprocal space for the kinetic energy and in real space for the pseudopotentials. Details about the implementation of this will be discussed in sec. II.2.2.

I.2 Density Functional Perturbation Theory

Within the framework of DFT a treatment of lattice vibrations can also be derived, as just knowledge of the ground-state density and its linear response to change in nucleic geometry is needed. As this is the fundamental quantity in DFT, an extension in DFPT can be developed for calculating properties of lattice vibrations. This theory will be outlined in this section, following the review article by Baroni et al. [12].

I.2.1 Sternheimer equation and Hellman-Feynman theorem

In a first step, two prerequisite equations are derived, namely the Sternheimer equation describing corrections to a wave function and the Hellman-Feynman theorem linking the derivative of the total energy of a system to the derivative of the Hamiltonian with regards to the same parameter.

The Sternheimer equation follows from standard perturbation theory. The idea of perturbation theory is to treat a quantum system as an easily solvable system $\hat{H}_0$ experiencing a small perturbation $\hat{H}_1$. The Hamiltonian for the perturbed system is then

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \tag{I.20}$$

with eigenstates und eigenvalues

$$\hat{H}\,|n\rangle = \epsilon_n\,|n\rangle\ . \tag{I.21}$$

These eigenstates and eigenvalues can now be expanded in terms of the parameter λ,

$$|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots , \tag{I.22}$$

$$\epsilon_n = \epsilon_n^{(0)} + \lambda\epsilon_n^{(1)} + \lambda^2\epsilon_n^{(2)} + \dots . \tag{I.23}$$

Inserting these expansion into eq. I.21 and sorting by order of λ^n gives then

$$0^{\text{th}} \text{ order:} \quad H_0 |n^0\rangle = \epsilon_n^{(0)} |n^0\rangle \tag{I.24}$$

$$1^{\text{st}} \text{ order:} \quad H_0 |n^1\rangle + H_1 |n^0\rangle = \epsilon_n^{(1)} |n^0\rangle + \epsilon_n^{(0)} |n^1\rangle \tag{I.25}$$

$$2^{\text{nd}} \text{ order:} \quad H_0 |n^2\rangle + H_1 |n^1\rangle = \epsilon_n^{(0)} |n^2\rangle + \epsilon_n^{(1)} |n^1\rangle + \epsilon_n^{(2)} |n^0\rangle \tag{I.26}$$

$$\vdots$$

Multiplying eq. I.25 with $\langle n^0|$ from the left leads then to the first order energy correction via

$$\langle n^0| H_0 |n^1\rangle + \langle n^0| H_1 |n^0\rangle = \epsilon_n^{(1)} \langle n^0|n^0\rangle + \epsilon_n^{(0)} \langle n^0|n^1\rangle \tag{I.27}$$

$$\implies \epsilon_n^{(1)} = \langle n^0| H_1 |n^0\rangle . \tag{I.28}$$

The first order correction to the eigenstates, also known as the *Sternheimer equation* can be calculated by rearranging eq. I.25

$$(H_0 - \epsilon_n^{(0)}) |n^1\rangle = -(H_1 - \epsilon_n^{(1)}) |n^0\rangle . \tag{I.29}$$

The Hellman-Feynman theorem [13] links the derivative of the eigenvalue of a Hamiltonian $\hat{H}_\lambda$ depending on a continuos parameter λ with the derivative of the Hamiltonian with respect to that same parameter. Starting from the Schrödinger equation

$$\hat{H}_\lambda |\psi_\lambda\rangle = E_\lambda |\psi_\lambda\rangle \tag{I.30}$$

the derivative of E_λ with respect to λ can be calculated using the product rule

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial}{\partial \lambda} \langle\psi_\lambda| \hat{H}_\lambda |\psi_\lambda\rangle \tag{I.31}$$

$$= \langle \frac{\partial \psi_\lambda}{\partial \lambda}| \hat{H}_\lambda |\psi_\lambda\rangle + \langle\psi_\lambda| \hat{H}_\lambda |\frac{\partial \psi_\lambda}{\partial \lambda}\rangle + \langle\psi_\lambda| \frac{\partial \hat{H}_\lambda}{\partial \lambda} |\psi_\lambda\rangle . \tag{I.32}$$

$\hat{H}_\lambda$ can now act on the states $|\psi_\lambda\rangle$ to the right or to the left in the first two terms

$$= E_\lambda \langle \frac{\partial \psi_\lambda}{\partial \lambda}|\psi_\lambda\rangle + E_\lambda \langle\psi_\lambda|\frac{\partial \psi_\lambda}{\partial \lambda}\rangle + \langle\psi_\lambda| \frac{\partial \hat{H}_\lambda}{\partial \lambda} |\psi_\lambda\rangle \tag{I.33}$$

$$= E_\lambda \frac{\partial}{\partial \lambda} \langle\psi_\lambda|\psi_\lambda\rangle + \langle\psi_\lambda| \frac{\partial \hat{H}_\lambda}{\partial \lambda} |\psi_\lambda\rangle \tag{I.34}$$

$$= E_\lambda \frac{\partial}{\partial \lambda} 1 + \langle\psi_\lambda| \frac{\partial \hat{H}_\lambda}{\partial \lambda} |\psi_\lambda\rangle . \tag{I.35}$$

With that the *Hellman-Feynman theorem* follows:

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle\psi_\lambda| \frac{\partial \hat{H}_\lambda}{\partial \lambda} |\psi_\lambda\rangle \tag{I.36}$$

I.2.2 Lattice vibrations from electronic structure

As discussed in the beginning of this chapter, nucleic and electronic degrees of freedom can be decoupled in the Born-Oppenheimer approximation. The connection between lattice dynamics and the electronic structure in the Born-Oppenheimer approximation was first pointed out by De Cicco and Johnson [14] and Pick, Cohen, Martin [15]. The lattice dynamics are determined by

$$\left(-\sum_{\alpha}\frac{1}{2M_\alpha}\nabla_\alpha^2 + E(\boldsymbol{R})\right)\Phi(\boldsymbol{R}) = \mathcal{E}\Phi(\boldsymbol{R})\,, \tag{I.37}$$

where $\boldsymbol{R}$ is the set of all nuclear coordinates $\boldsymbol{R}_\alpha$ and $E(\boldsymbol{R})$ is the ground-state energy of the electronic Hamiltonian I.4, which depends parametrically on $\boldsymbol{R}$. The system is then in equilibrium, when the forces acting on the nuclei vanish

$$\boldsymbol{F}_\alpha = -\frac{\partial E(\boldsymbol{R})}{\partial \boldsymbol{R}_\alpha} = 0\,. \tag{I.38}$$

The vibrational frequencies ω are determined by the Hessian of $E(\boldsymbol{R})$, usually called the matrix of interatomic force constants:

$$\det\left|\frac{1}{\sqrt{M_\alpha M_\beta}}\frac{\partial^2 E(\boldsymbol{R})}{\partial \boldsymbol{R}_\alpha \partial \boldsymbol{R}_\beta} - \omega^2\right| = 0\,. \tag{I.39}$$

Thus the calculation of the vibrational properties as well as the equilibrium geometry depend on the first and second derivatives of the energies $E(\boldsymbol{R})$. These derivatives can be calculated using the Hellman-Feynman theorem I.36, where the parameter λ is the nucleic coordinate $\boldsymbol{R}_\alpha$. Keeping in mind that in the Born-Oppenheimer Hamiltonian I.4 only the Coulomb interaction between the electrons and the nuclei and the Coulomb interaction between the nuclei have a dependence on the nucleic coordinates $\boldsymbol{R}$, the force acting on nucleus α is then

$$\boldsymbol{F}_\alpha = -\frac{\partial E(\boldsymbol{R})}{\partial \boldsymbol{R}_\alpha} = -\left\langle \Psi_{\boldsymbol{R}}(\boldsymbol{r}) \middle| \frac{\partial \hat{H}_{\mathrm{BO}}(\boldsymbol{R})}{\partial \boldsymbol{R}_\alpha} \middle| \Psi_{\boldsymbol{R}}(\boldsymbol{r}) \right\rangle \tag{I.40}$$

$$= -\left\langle \Psi_{\boldsymbol{R}}(\boldsymbol{r}) \middle| \frac{\partial \hat{V}_{\mathrm{n-e}}}{\partial \boldsymbol{R}_\alpha} + \frac{\partial \hat{W}_{\mathrm{n-n}}}{\partial \boldsymbol{R}_\alpha} \middle| \Psi_{\boldsymbol{R}}(\boldsymbol{r}) \right\rangle \tag{I.41}$$

$$= -\int \mathrm{d}\boldsymbol{r}\, n_{\boldsymbol{R}}(\boldsymbol{r}) \frac{\partial V_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\alpha} - \frac{\partial W_{\mathrm{n-n}}}{\partial \boldsymbol{R}_\alpha}\,, \tag{I.42}$$

where $n_{\boldsymbol{R}}(\boldsymbol{r})$ is the ground state electronic density corresponding to a nucleic configuration $\boldsymbol{R}$. The second derivative of $E(\boldsymbol{R})$ is then calculated using the product rule

$$\frac{\partial^2 E(\boldsymbol{R})}{\partial \boldsymbol{R}_\alpha \partial \boldsymbol{R}_\beta} = -\frac{\partial \boldsymbol{F}_\alpha}{\partial \boldsymbol{R}_\beta} = \int \mathrm{d}\boldsymbol{r}\, \frac{\partial n_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\beta}\frac{\partial V_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\alpha} + \int \mathrm{d}\boldsymbol{r}\, n_{\boldsymbol{R}}(\boldsymbol{r})\frac{\partial^2 V_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\alpha \partial \boldsymbol{R}_\beta} + \frac{\partial^2 W_{\mathrm{n-n}}}{\partial \boldsymbol{R}_\alpha \partial \boldsymbol{R}_\beta}\,. \tag{I.43}$$

The lattice dynamics are thus determined by the electronic density $n(\boldsymbol{r})$ and its linear response to a change in the nuclear geometry $\frac{\partial n_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\beta}$.

I.2.3 Density Functional Perturbation Theory

The density response $\frac{\partial n_{\boldsymbol{R}}(\boldsymbol{r})}{\partial \boldsymbol{R}_\beta}$ can be calculated within a KS DFT formulation. This approach combining perturbation theory, linear response theory and DFT is called Density Functional Perturbation Theory (DFPT), developed by Baroni et al. [16] and Gonze [17].

In a first step, the electronic density I.8 will be linearized

$$\Delta n(\boldsymbol{r}) = 4\,\mathrm{Re}\left\{\sum_i^{N_e/2} \Psi_i^*(\boldsymbol{r})\Delta\Psi_i(\boldsymbol{r})\right\} \tag{I.44}$$

with the finite-difference operator regarding the parameter $\boldsymbol{R}$ (the subscript has been omitted in eq. I.44)

$$\Delta^{\boldsymbol{R}} F = \sum_\alpha \frac{\partial F_{\boldsymbol{R}}}{\partial \boldsymbol{R}_\alpha}\Delta\boldsymbol{R}_\alpha\,. \tag{I.45}$$

The variation of the KS orbitals can be obtained with the Sternheimer equation I.29

$$(H_0 - \epsilon_i)\,|\Delta\Psi_i\rangle = -(\Delta v_{\mathrm{KS}} - \Delta\epsilon_i)\,|\Psi_i\rangle\ , \tag{I.46}$$

where H_0 is the unperturbed KS Hamiltonian I.7, Δv_{KS} is the first-order correction to the potential v_{KS}

$$\Delta v_{\mathrm{KS}} = \frac{1}{2}\int \mathrm{d}^3 r' \,\frac{\Delta n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \left.\frac{\partial v_{\mathrm{XC}}}{\partial n}\right|_{n=n(\boldsymbol{r})} + \Delta V \tag{I.47}$$

and $\Delta\epsilon_i = \langle\Psi_i|\Delta v_{\mathrm{KS}}|\Psi_i\rangle$ is the first-order correction to the KS eigenvalue ϵ_i.

As the right hand site in eq. I.46 depends again on the perturbed density $\Delta n(\boldsymbol{r})$ (and as such on $|\Delta\Psi_i\rangle$), eq. I.44-I.47 are again self consistent equations, which can be solved in an iterative manner.

II Computational Details

II.1 Parallel computing

The following section will give an overview of the technical aspects of running computer code (such as Quantum ESPRESSO) on massively parallel computing environments (such as the PHYSnet compute cluster). The information presented in this section comes from the textbook on high-performance computing by Hager and Wellein [18].

II.1.1 On scalabilty

In scientific computing, one can identify two distinct reasons for distributing workloads to multiple processors:

- The execution time on a single core is not sufficient. The definition of sufficient is dependent on the specific task and can range from "over lunch" to "multiple weeks".
- The memory requirements grow outside the capabilities of a single core.

In order to judge how well a task can be parallelized, usually a scalability metric is employed, for example:

- How fast can a problem be solved with N processors instead of one?
- What kind of bigger problem (finer resolution, more particles, etc.) can be solved with N processors?
- How efficiently are the resources utilized?

In this thesis, the main concern is speeding up the execution of extensively expensive calculations with a fixed problem size, so the first metric will be used to judge the quality of parallelization. This metric is called speedup and is defined as

$$S = \frac{T_1}{T_N}\,, \tag{II.1}$$

where T_1 is the execution time on a single processor and T_N is the execution time on N processors. In the ideal case, where all the work can be perfectly distributed among the processors, all processors need the same time for their respective workloads and don't depend on others processors finishing their workload to continue, the execution time on N processors would be $\frac{T_1}{N}$, so inserting this into eq. II.1 gives a speedup of

$$S = \frac{T_1}{\frac{T_1}{N}} = N\,. \tag{II.2}$$

In reality, there are many factors either limiting or in some cases supporting parallel code scalability. Limiting factors include:

- *Algorithmic limitations*: when parts of a calculation are mutually dependent on each other, the calculation cannot be fully parallelized
- *Bottlenecks*: in any computer system exist resources which are shared between processor cores with limitations on parallel access. This serializes the execution by requiring cores to wait for others to complete the task which uses the shared resources in question
- *Startup Overhead*: introducing parallelization into a programm necessarily introduces an overhead, e.g. for distributing data across all the processors
- *Communication*: often solving a problem requires communication between different cores (e.g. exchange of interim results after a step of the calculation). Communication can be implemented very effectively, but can still introduce a big prize in computation time

On the other hand, *better caching* can lead to better scaling than $S = N$: as optimal performance per core is achieved when all the data can be kept in cache, reducing the data size per processor by distributing data among more processors can lead to each individual processor being faster than in the single core case.

A simple ansatz for modeling speedup with these limitations in mind was first derived by Gene Amdahl [19]. Assuming the work that needs to be done is split into a part which cannot be parallelized s and a part which can be parallelized ideally p, serial time can be normalized to 1:

$$T_1 = s + p = 1 \tag{II.3}$$

The time for solving the problem on N processors is then

$$T_N = s + \frac{p}{N}\,. \tag{II.4}$$

The speedup is now

$$S = \frac{T_s}{T_p} = \frac{1}{s + \frac{p}{N}} = \frac{1}{s + \frac{1-s}{N}} \tag{II.5}$$

This equation is called *Amdahl's law* and is plotted in fig. ?? over a range of processors for a few different values of s.

II.1.2 Evaluating the scalability of Quantum ESPRESSO calculations

In the Quantum ESPRESSO output, a time report listing is printed at the end. This time report includes CPU time and wall time, from those three different metrics of scalability can be calculated:

- runtime: absolute runtime (wall time) of the compute job
- speedup: runtime on N processors divided by runtime on a single core
- wait time: percentage of wall time not used by Quantum ESPRESSO process, so writing to disk, waiting for IO devices or other processes, etc. (calculated as (wall time - CPU time) / wall time)

For analysis mainly speedup will be used to evaluate the scalability of Quantum ESPRESSO calculation. It makes comparing the scaling of calculations with different absolute runtimes easy: as discussed in sec. II.1.1, optimal scaling is achieved when the speedup has a slope of one, independent of the runtime.

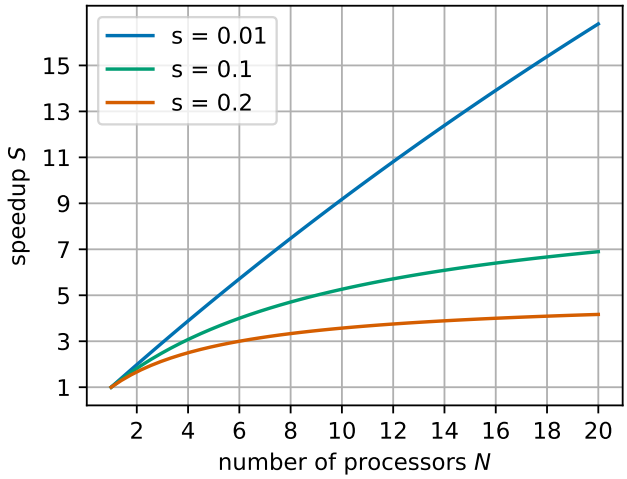


Figure II.1: *Amdahl's law for different portions of not parallelizable workload s*

Regardless, the other two parameters should also always be considered: in the end, absolute runtime is the most important factor and should govern the decision of how much resources are used for solving a particular problem. For instance, a problem with a single core runtime of 600 s, a speedup of 100 would mean a runtime of 6 s, whereas a speedup of 200 would mean a runtime of 3 s. Even with optimal scaling, the 100 processors needed for the speedup of 200 could be considered wasted for just 3 s of saved time. On the other hand, for a problem with a single core runtime of 2400 h, the difference between a speedup of 100 (runtime 24 h) and 200 (runtime 12 h) is the difference between needing to wait a whole day for the calculation and being able to let the job run overnight and continue working in the morning, so using 100 more processors for that can be considered a good use of resources.

As for the wait time, this metric can be used to separate the different factors of poor parallelization discussed in II.1.1. Startup overhead is easy to identify, as this should be a small, near constant percentage of the absolute runtime. This of course can vary depending on how complex data distribution is, but there should at least not be a strong dependence on the number of processors, as only a small amount of communication is needed. Communication and bottlenecks on the other hand both introduce wait time which depends on the number of processors. Differentiating between them is relies on knowledge of the specific hardware of the system running the calculations, so how many cores are on a single chip, motherboard or node, which resources are shared between how many cores, etc..

For this interpretation to be meaningful, the CPU and wall times reported by Quantum ESPRESSO have to be accurate, because they are trusted without verification. Just as an example for the pitfalls of this approach, when executing programs on multiple processors in parallel, CPU time is measured per processor, so some kind of truncation is done when a single number (such as in Quantum ESPRESSO) is reported. Whether this is taking the average over all processors, just reporting the time for a single processor or any other kind of truncation is unclear.

However, the notion of using the difference between wall time and CPU time for evaluating the quality of parallelization is supported by the user guide for one of the QUANTUM ESPRESSO modules [20] (sec. 4.5), therefore it will also be used as a qualitative measure of good parallelization in this thesis.

II.2 Quantum ESPRESSO

QUANTUM ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) [4, 5] is a collection of packages implementing (among others) the techniques described in sec. I.1 and **??** to calculate electronic structure properties (module `PWscf`) as well as phonon frequencies and eigenmodes (module `PHonon`).

II.2.1 Compilation of Quantum ESPRESSO

As the core of this thesis is an in depth examination of the QUANTUM ESPRESSO software and ways its performance can be optimized, a discussion of the way it is compiled is needed. The information in this section is taken from the QUANTUM ESPRESSO 7.0 user guide [21].

The QUANTUM ESPRESSO distribution is packaged with everything needed for simple, non-parallel execution, the only additional software needed are a minimal Unix environment (a shell like `bash` or `sh` as well as the utilities `make` `awk` and `sed`) and a Fortran compiler compliant with the F2008 standard. For parallel execution, also MPI libraries and an MPI aware compiler need to be provided.

QUANTUM ESPRESSO needs three external mathematical libraries, BLAS and LAPACK for linear algebra as well as an implementation of FFT for fourier transforms. In order to make the installation as easy as possible, QUANTUM ESPRESSO comes with a publicly available reference implementation of the BLAS routines, the publicly available LAPACK package and an older version of FFTW (Fastest Fourier Transform in the West, an open source implementation of FFT). Even though these libraries are already optimized in terms of the algorithms implemented, usage of libraries implementing the same routines which can use more specific CPU optimizations significantly improves performance (e.g. libraries provided by Intel can use CPU optimizations not present on AMD processors).

On the PHYSnet cluster, a variety of software packages are available as modules. The benchmarks in this thesis were made using the following module combinations:

- `openmpi/4.1.1.gcc10.2-infiniband`: OpenMPI 4.1.0 (implies usage of QUANTUM ESPRESSO provided BLAS/LAPACK)
- `openmpi/4.1.1.gcc10.2-infiniband openblas/0.3.20`: OpenMPI 4.1.0 and OpenBLAS 0.3.20
- `scalapack/2.2.0`: OpenMPI 4.1.0, OpenBLAS 0.3.20 and ScaLAPACK 2.2.0
- `intel/oneAPI-2021.4`: Intel oneAPI 2021.4

QUANTUM ESPRESSO offers a configuration script to automatically find all required libraries. As the default options of the `configure` script work well in the use case of this thesis, all compilations were made using the minimal commands

```
module load <module names>
./configure --with-scalapack=no|yes|intel
```

with the scalapack options yes (when using `scalapack/2.2.0`), intel (when using `intel/oneAPI-2021.4`) and no otherwise.

The output of the configuration script gives information about the detected libraries. In the following output, the Intel Intel oneAPI package was loaded, so BLAS and ScaLAPACK libraries from that package will be used, whereas the included FFT library will be used:

```
The following libraries have been found:
BLAS_LIBS=  -lmkl_intel_lp64  -lmkl_sequential -lmkl_core
LAPACK_LIBS=
SCALAPACK_LIBS=-lmkl_scalapack_lp64 -lmkl_blacs_intelmpi_lp64
FFT_LIBS=
```

II.2.2 Parallelization capabilities implemented in Quantum ESPRESSO

QUANTUM ESPRESSO is intended to be used in parallel environments and as such offers possibilities to manage how the work is parallelized. This section introduces the parallelization capabilities of the `PWscf` and `PHonon` modules and explores how they potentially affect the scaling behavior of QUANTUM ESPRESSO. The information in this section stems from the user guides for the two modules [20, 22]

Fig. ?? shows a possible approach to solving the KS equations. A few possibilities for parallelization of calculations can be derived from that.

First of all, the real/reciprocal are discretized to allow for numerical treatment, these grids can be distributed among processors, meaning the orbitals in the plane wave basis set as well as charges and densities. This distribution of data mainly works around memory constraints, as using more processors lowers the memory requirement for every single processor. Going further, QUANTUM ESPRESSO automatically parallelizes all linear algebra operations on this real space/reciprocal grid. The price to pay for this parallelization is the need for communication between processors: as an example, fourier transforms always need to collect and distribute contributions from and to the whole reciprocal/real grid in order to transform between them. This kind of parallelization is called *PW (plane wave)* or *R&G (real & reciprocal)* parallelization.

As discussed in sec. I.1.3, the density in the plane wave basis set is a sum over different k points, where the calculation for these are independent of each other until calculating the density $n(\boldsymbol{r})$. In QUANTUM ESPRESSO this is implemented such that a separation of the total number of processors into smaller pools, each doing the calculations for a set of k points is possible. This is called *k point parallelization*. The CLI parameter `-nk <number of pools>` determines how many pools the total number of processor N is split into. Hence, the resulting number of processors in one pool is N/N_k. Within one k point processor pool, the PW parallelization with its heavy communication is automatically applied.

In a level of parallelization independent of that, QUANTUM ESPRESSO can use ScaLAPACK to parallelize (among other things) the iterative orthonormalization of KS states. This parallelization level is called *linear algebra parallelization* and is controlled by the CLI parameter

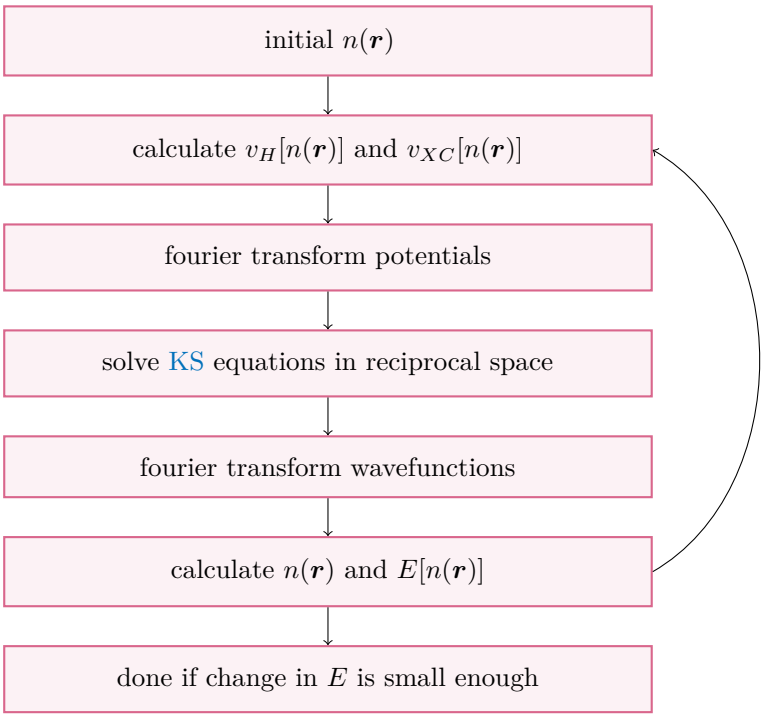


Figure II.2: *Flowchart of an algorithm to iteratively solve the KS equations with the use of fourier transform*

`-nd <number of processors in linear algebra group>`. Importantly, this parameter sets the size for the linear algebra group in every k point processor pool, so the number of processors in the linear algebra group has to be smaller than the number of processors in one pool. Furthermore, the arrays on which the calculations are performed on are distributed in a 2D grid among processors, so the number of processors in the linear algebra group has to be a square number.

In the case of the `PHonon` module, the representation of states in a plane-wave basis set stays the same, so all three parallelization schemes mentioned for the `PWscf` module can also be employed. Furthermore, as calculations for two phonon wave vectors $\boldsymbol{q}, \boldsymbol{q}'$ are not coupled (as different wave vectors lead to different perturbations and as such independent self-consistent equations), they can be split up into images. The concept of image parallelization in QUANTUM ESPRESSO is actually more general than just for phonon calculations, as other kinds of independent iterative calculations can also be run with image parallelization. The parameter controlling image parallelization is `ni <number of images>`. Following this, the number of processors in one k point pool is then given by $N/N_i/N_k$.

II.3 Hardware configuration of the PHYSnet cluster

All calculations were run on a reserved subset of the `infinix` queue on the PHYSnet compute cluster, with 20 nodes. As of time of writing, the nodes in this queue are equipped with two Intel Xeon E5-2680 CPUs, as such providing 20 cores per node, 10 per chip and 200 processors in the whole queue.

speed comparison

II.4 Examined systems

II.4.1 Silicon

Silicon is the fundamental material in integrated circuits and as such is one of the pillars of the digital revolution. Analogue to the Stone, Bronze or Iron Age, this age of civilization can thus be called the Silicon Age [23]. Consequently, silicon is a well studied material from an experimental and theoretical standpoint with established properties. This combined with the fact that with only 8 electrons per unit cell DFT calculations on silicon are not particularly expensive makes it an ideal system for many introduction to DFT calculation as well as a good benchmarking system. All benchmarks in this thesis were run on silicon first and with the information gained from that benchmarks on a more expensive system were run.

crystal structure?

The calculations in ch. III were made with a plane wave cutoff of

made on a 40x40x40 k point grid,

All calculations use a PBE XC-functional with a norm-conserving PP generated using Vanderbilt's method [24].

II.4.2 TaS_2

III Parallelization of electronic-structure calculations

The `PWscf` (Plane-Wave Self-Consistent Field) package is one of the core modules of QUANTUM ESPRESSO, as many other modules need ground state density and total energy as input. This chapter deals with examining the best ways to run `PWscf` calculations in the `scf` mode.

III.1 First scaling tests

The first step in analyzing the scaling of the `PWscf` module is to perform a baseline scaling test without any optimizations applied. In Fig. III.1 to III.4 two scaling tests on the earlier mentioned benchmarking systems Si and TaS_2 are depicted. The tests are run using QUANTUM ESPRESSO 7.0, compiled using the Fortran and C compilers in OpenMPI 4.1.0, without any of the compilation or runtime optimization parameters mentioned in section II.2 used.

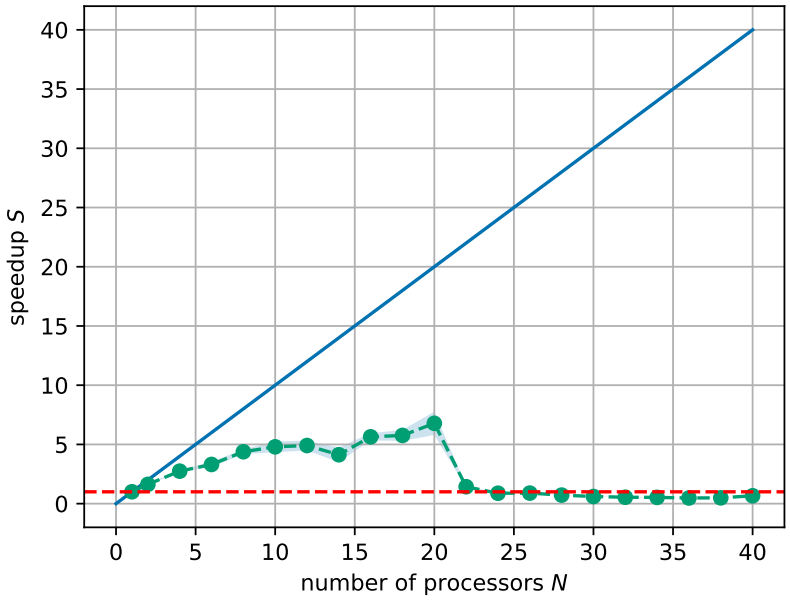


Figure III.1: *Scalability for the Si benchmarking system,* QUANTUM ESPRESSO 7.0, OpenMPI 4.1.0, `nk 1` and `nd 1`

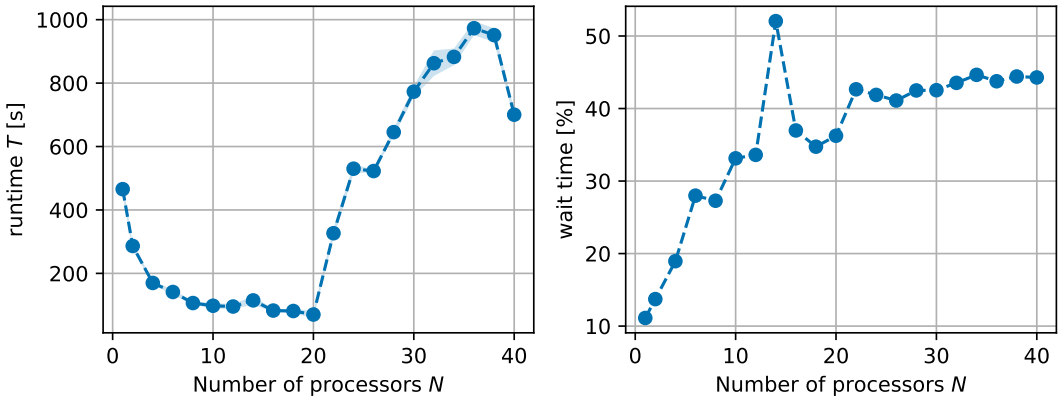


Figure III.2: *Absolute runtime and wait time for the scalability test on the Si benchmarking system,* Quantum ESPRESSO compiled with OpenMPI 4.1.0, `nk 1` and `nd 1`

As discussed in sec. II.1.2, three different metrics of scalability can be deduced from the time data given by Quantum ESPRESSO:

- runtime: absolute runtime (walltime) of the compute job
- speedup: runtime divided by runtime of the job on a single core
- wait time: percentage of wall time used by system tasks, e.g. writing to disk, etc.

These are depicted in fig. III.1 and III.2 for the silicon benchmarking system.

On a single node, the speedup does scale linearly with the number of processors until around 10 processors, but with a slope of $\frac{1}{2}$ instead of 1 (which would mean ideal scaling). Beyond that number, the slope decreases even more so that a maximal speedup of around 7 is achieved for 20 processors used. One compute node is equipped with 20 cores, so trying to scale the communication intensive calculations beyond that threshold makes the calculations run even slower than on a single core. Interestingly, the wait time plot in III.2 shows that a significant amount (10 % to 40 %) of runtime is taken up by wait time already for less than 20 processors. As discussed in sec. II.1.1, this is a sign of poor parallelization, which can explain the poor scaling seen in fig. III.1.

shown in fig. III.3 and III.4 are the same scaling test run for the TaS_2 benchmarking system. Here, the speedup is not taken as runtime divided by runtime on a single core, as the memory required is more than what can be accessed by a single core. Instead, an estimate of the single core runtime is made by multiplying the runtime of the job running on 4 cores by 4. This assumes perfect scaling for 1-4 processors, but the relative scaling is accurate, no matter the accuracy of this assumption.

The scaling test on the TaS_2 system shows much better scaling. For up to 20 processors, the speedup follows the ideal scaling with a stark decline with more processors. This is also reflected in the wait time in fig. III.4, as it goes from a small constant value for under 20 processors to some kind of dependence of the number of processors, which hints to communication or bottlenecks being a limiting factor here.

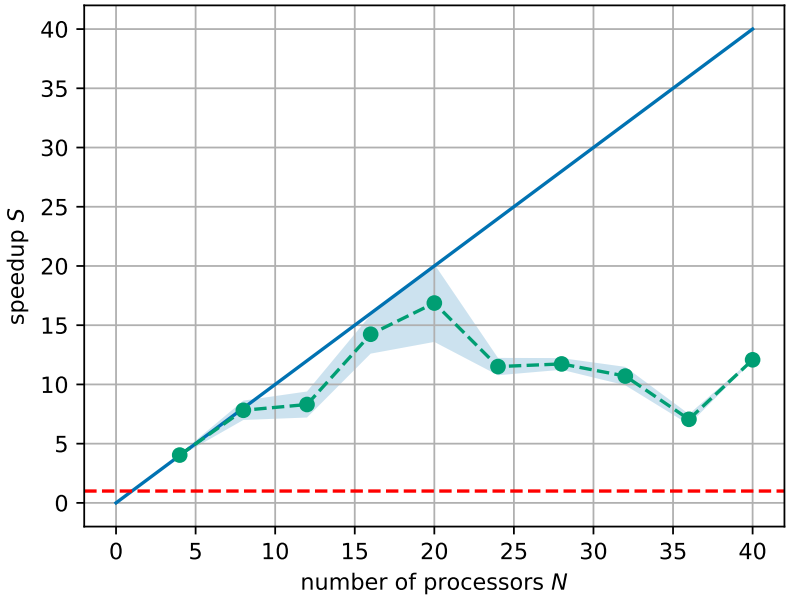


Figure III.3: *Scalability for the TaS_2 benchmarking system,* Quantum ESPRESSO 7.0, OpenMPI 4.1.0, `nk 1` and `nd 1`

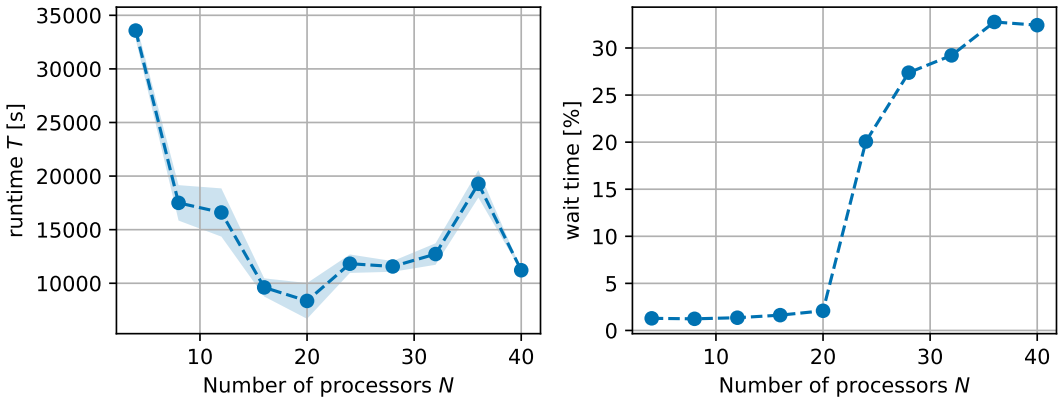


Figure III.4: *Absolute runtime and wait time for the scalability test on the TaS_2 benchmarking system,* Quantum ESPRESSO 7.0, OpenMPI 4.1.0, `nk 1` and `nd 1`

In conclusion, systems with more electrons and by extension bigger matrices and longer iteration times seem to be parallelize better and as such profit more from using more processors than systems with just a few number of electrons.

These scaling tests now pose the question how better scaling over more than one node can be achieved.

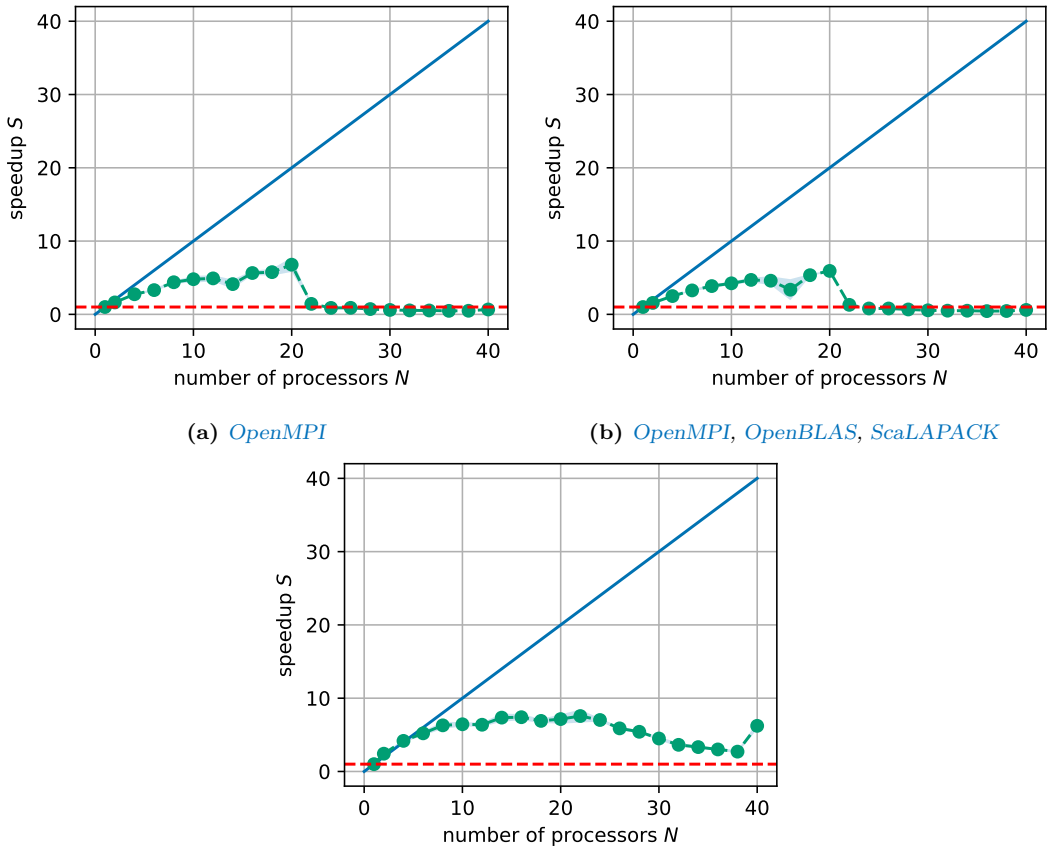
III.2 Testing different compilers and mathematical libraries

A first strategy for solving issues with parallelization is trying different compilers and mathematical libraries. As discussed in sec. II.2.1, QUANTUM ESPRESSO can make use of a variety of software packages available on the PHYSnet cluster. The benchmarks in **??** are run with the following software combinations:

(a) OpenMPI 4.1.0 and QUANTUM ESPRESSO provided BLAS/LAPACK, so the baseline test discussed in sec. III.1

(b) OpenMPI 4.1.0, OpenBLAS 0.3.20 and ScaLAPACK 2.2.0

(c) Intel oneAPI 2021.4

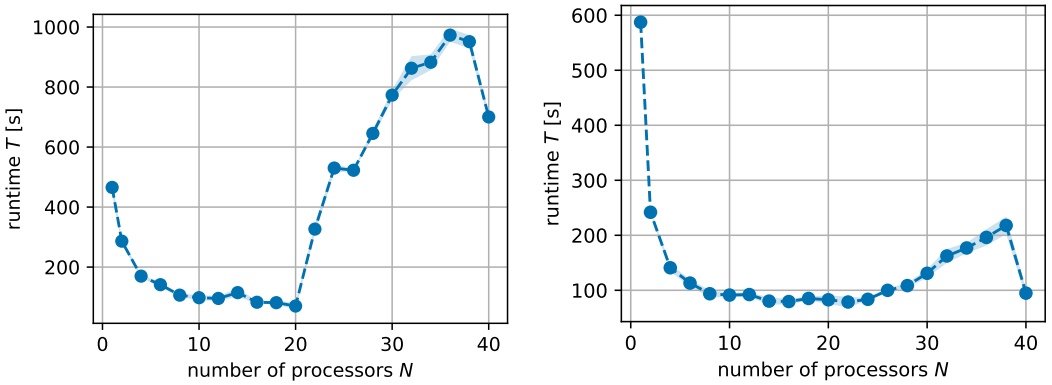


(a) *OpenMPI* **(b)** *OpenMPI*, *OpenBLAS*, *ScaLAPACK*

(c) *Intel oneAPI*

Figure III.5: *Scalability for the Si benchmarking system with different combinations of compilers and mathematical libraries,* `nk 1` and `nd 1`

Fig. **??** shows that just using another BLAS/LAPACK library (OpenBLAS in this case) with the same MPI version does not change the scaling behavior, in contrast to using Intels Intel oneAPI packages. Here, optimal scaling behavior is seen for up to 6 processors. It is however important to also look at the total runtime in this context.



(a) *OpenMPI 4.1.0* **(b)** *Intel oneAPI 2021.4*

Figure III.6: *Comparison of absolute runtimes between* Quantum ESPRESSO *compiled with OpenMPI and Intel oneAPI for the Si benchmarking system,* `nk 1` and `nd 1`

Fig. **??** shows the absolute runtime for both the OpenMPI and Intel oneAPI benchmarks. This explains the difference in scaling seen in the speedup plots: the runtime on a single core is significantly higher for the Intel oneAPI benchmark, so even though the runtime between both benchmarks is about the same starting from around 10 processors there is a difference in speedup. To assess this more quantitatively, tab. III.1 lists the average runtime for some selected number of processors. Importantly, the runtime for the Intel oneAPI benchmark is faster for smaller numbers of processors (except 1), but only 15 % for 2 cores and even smaller differences for more cores, with the OpenMPI calculation being even a little faster for 20 processors.

Table III.1: *Selected absolute runtimes of* Quantum ESPRESSO *compiled with OpenMPI 4.1.0 and Intel oneAPI 2021.4 for the Si benchmarking system,* `nk 1` and `nd 1`

Number of processors	OpenMPI	Intel oneAPI
1	466 s	587 s
2	286 s	242 s
4	170 s	141 s
10	97.9 s	91.3 s
20	70.2 s	82.8 s

The same benchmark with the Intel oneAPI compiled version of Quantum ESPRESSO is shown in fig. III.7 and III.8. For this system, the speedup roughly follows Amdahl's law, discussed in sec. II.1.1 with a linear growth in speedup up to 32 processors with a saturation

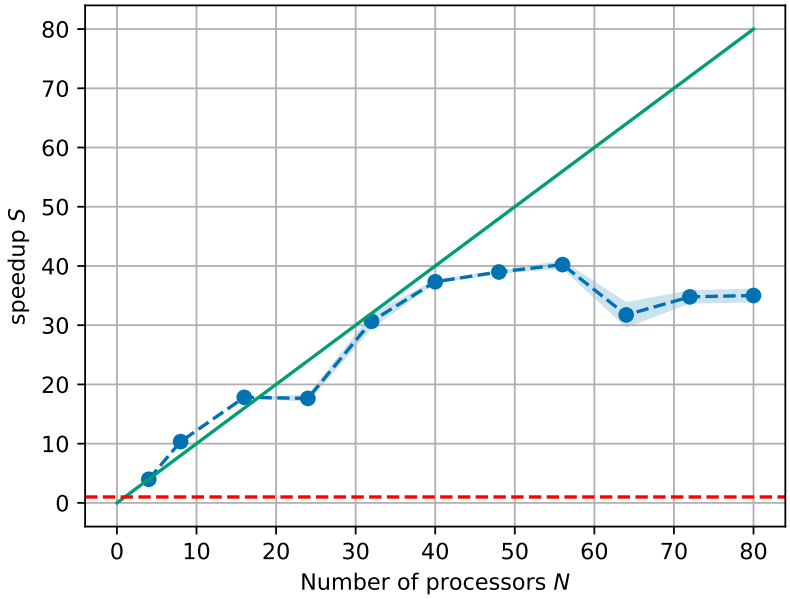


Figure III.7: *Scalability for the TaS_2 benchmarking system,* QUANTUM ESPRESSO 7.0 compiled with Intel oneAPI 2021.4, `nk 1` and `nd 1`

and only a small gain in speedup with more processors. In contrast to the benchmark with just OpenMPI (fig. III.3) there is no drop in speedup after 20 processors. This is remarkable and also a difference to the silicon benchmarking system, where 1 node is a definite upper bound for scalability. An explanation for this behavior can be made with the help of Amdahl's law again. As discussed in sec. II.1.1, the exact form of the speedup is not dependent on absolute times of parallelized and unparallelized parts of a calculations, but rather the proportion between these two (and can thus be characterized by just the purely serial part s). This means that for a more expensive system such as the TaS_2 benchmarking system, when the absolute time for communication, data distribution and collection stays roughly the same and the time for a single Kohn-Sham (KS) iteration (which can be parallelized) is way longer, the proportion of the purely serial part s gets smaller and the scaling behavior changes significantly.

Moreover, the absolute runtime shown in fig. III.8 shows that the calculations not just scale better than with OpenMPI, but they are significantly faster: whereas the minimum for the OpenMPI benchmark is around 1 h 50 min for 20 processors, the Intel oneAPI benchmark averages around 40 min for 24 processors. While the benchmarks on the silicon benchmarking system do not seem to favor one set of compilers over the other, the tests on the TaS_2 benchmarking system clearly show the advantages of using Intel oneAPI on the Intel hardware in the PHYSnet cluster.

wait time tas2

The observations on how many processors are optimal for certain kinds of systems not only stand for themselves as a statement about scaling on a single node or a small number of nodes, but also provide a basis for scaling beyond the respective optimal ranges of processors for both systems: The k point parallelization explained in sec. II.2.2 can distribute the workload in

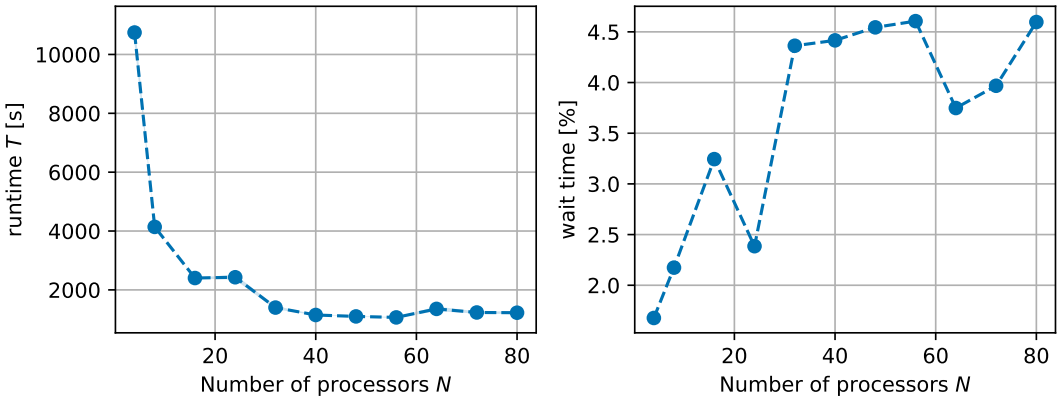


Figure III.8: *Absolute runtime and wait time for the scalability test on the TaS_2 benchmarking system,* QUANTUM ESPRESSO compiled with Intel oneAPI 2021.4, `nk 1` and `nd 1`

such a way that processor pools of sizes within this range work on individual k points and as such can provide optimal scaling within one pool while also not losing performance because the pools do not need to communicate with each other in the same order of magnitude as the pools have to communicate within themselves.

Keeping the results of this section in mind, an estimate for the quality of k point parallelization can already be made: For the silicon system, the size of pools should not be bigger than 6 processors for optimal scaling and for the TaS_2 system they should not be bigger than 32 processors.

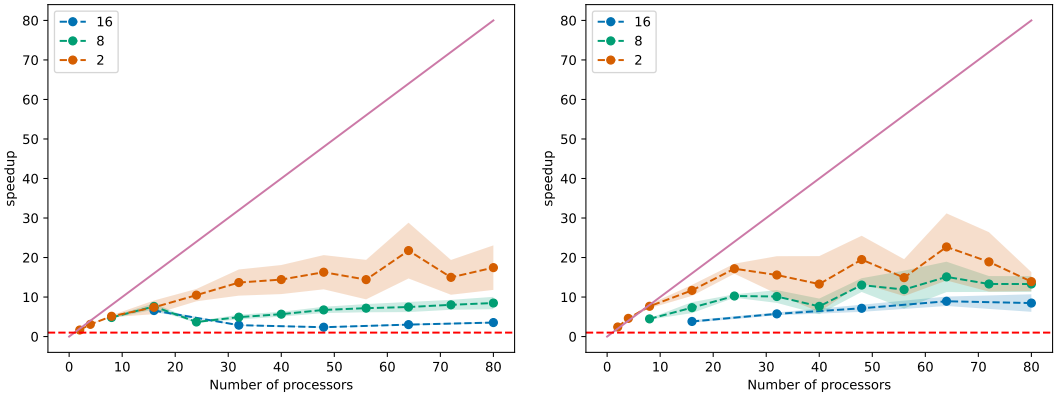
III.3 Using the parallelization parameters of Quantum ESPRESSO

As detailed in section II.2.2, QUANTUM ESPRESSO offers ways to manage how the workload is distributed among the processors. In `pw.x` the default plane wave parallelization, k point-parallelization and linear-algebra parallelization are implemented. While plane wave parallelization is automatically applied, k point and linear algebra parallelization can be controlled and will be tested in this section.

III.3.1 k point parallelization

The benchmark shown in III.9 is set up as follows: for a given number of processors N_p, the parameter N_k splits the N_p processors into N_k processors pools. As the number of processors in one pool has to be a whole number, only certain combinations of N_p and N_k are possible, for example $N_p = 32$ could be split into processor pools of size 2 with $N_k = 16$, size 8 with $N_k = 4$ or size 16 with $N_k = 2$. This leads to choosing the size of the processor pools as a variable, not the parameter `nk`.

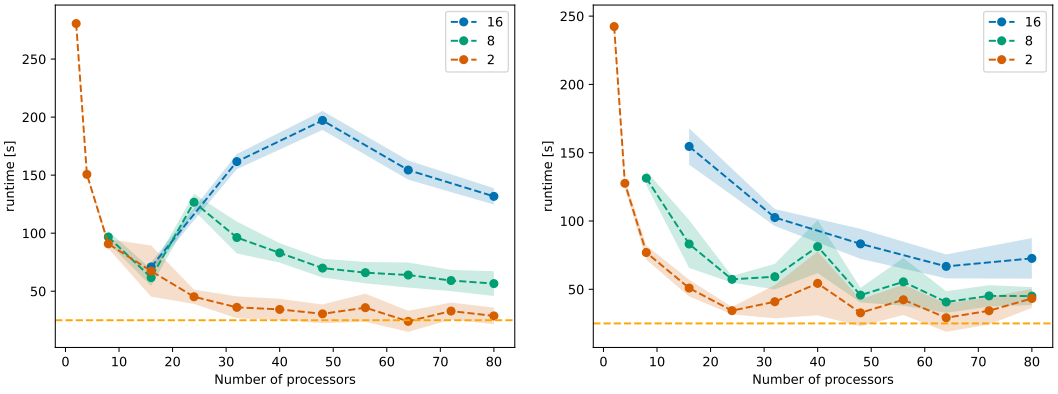
Fig. III.9 shows the scaling for poolsizes 2, 8 and 16 for QUANTUM ESPRESSO being compiled with OpenMPI and Intel oneAPI.



(a) *OpenMPI 4.1.0* **(b)** *Intel oneAPI 2021.4*

Figure III.9: *Scalability utilizing k-point parallelization for the Si benchmarking system with 3 different sizes of processor pools. The size is determined by the parameter* `nk` *via* size of pools = number of processors / nk

The speedup depicted in fig. III.9 shows that using k parallelization with a pool size of 2 improves the scaling behavior not only on one node, but especially over more than one node. While the speedup without k point parallelization hit a plateau when using more than 6 processors, k point parallelization enables scaling up until 24 processors. The bigger pool sizes do not scale as well, which is in agreement with the results of the benchmarks without k point parallelization presented in the previous section.



(a) *OpenMPI 4.1.0* **(b)** *Intel oneAPI 2021.4*

Figure III.10: *Absolute runtime for the scalability test with k-point parallelization for the Si benchmarking system with 3 different sizes of processor pools,* `nd 1`

The runtime shown in fig. III.10 show that the choice between using OpenMPI and Intel oneAPI does not result in a big difference in total execution time, in accordance For both benchmarks, the ideal number of processors seems to be around 24, after that the runtime is subject to significant fluctuations and does not decrease in a predictable way. The average runtime for 24 processors are 45.2 s (OpenMPI) and 34.4 s (Intel oneAPI) respectively, so about a 10 seconds difference and also around half the minimal time (70.2 s and 82.8 s at 20 processors) in comparison to the benchmark without k point parallelization.

The same scaling test is applied to the TaS_2 benchmarking system in fig. III.11 and III.12.

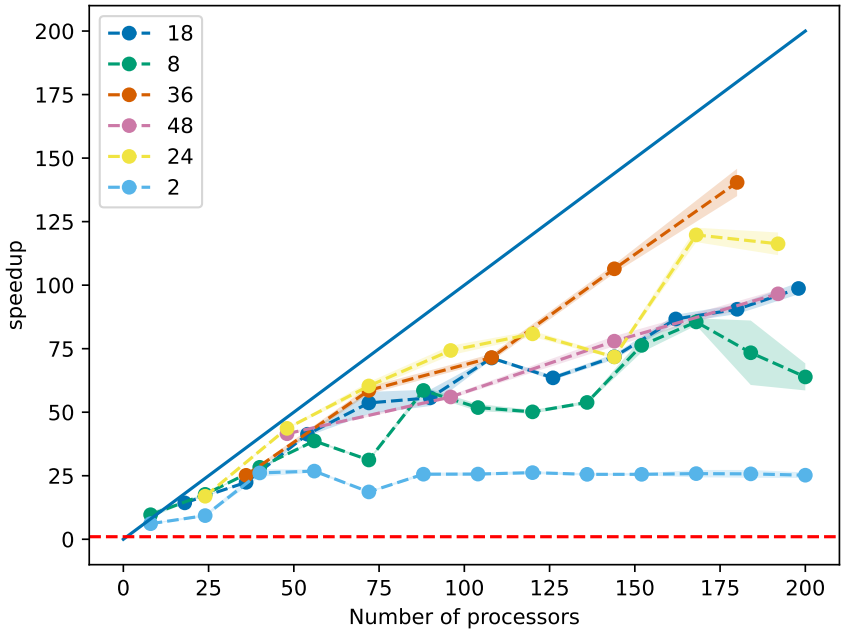


Figure III.11: *Scalability utilizing k-point parallelization for the TaS_2 benchmarking system over a range of processor pools,* QUANTUM ESPRESSO compiled with Intel oneAPI 2021.4, `nd 1`

Remarkably, the scaling behavior is swapped in comparison to fig. III.9, as the pool size 2 saturates and the bigger pool sizes show way better scaling behavior. As already alluded to in sec. III.2, the calculations on the TaS_2 system profit more from parallelization and as such scale better for bigger pool sizes up until 36 processors in one pool, which is around the upper limit established in the benchmark without k point parallelization.

analyse runtimes TaS2 nk

Fig. **??** shows a distribution of wait times between about 4 % and 6 % of the whole wall time, with a slight overall increase when going over 160 processors. This suggests very good parallelization across the whole range of processors.

III.3.2 Linear algebra parallelization

Fig. **??** shows the scaling behavior for different values of the parameter `nd`. Here, nd_auto means that no value for `nd` is specified so QUANTUM ESPRESSO automatically chooses the

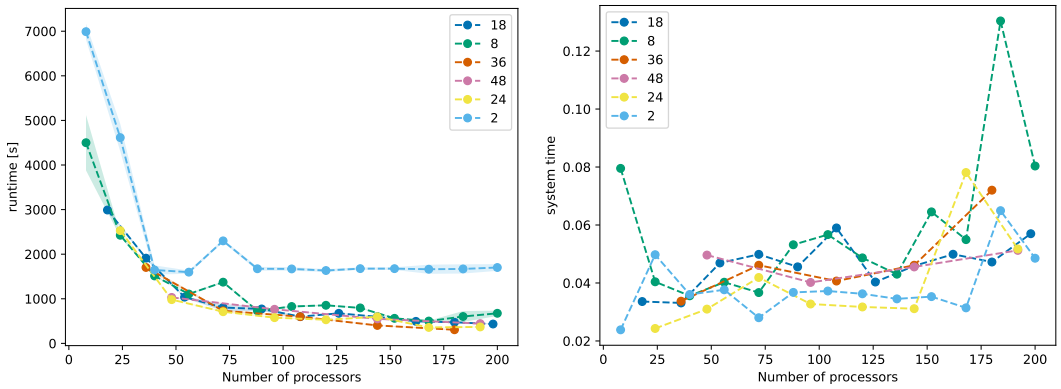


Figure III.12: *Absolute runtime and wait time for the scalability test with k-point parallelization for the TaS_2 benchmarking system over a range of processor pools,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nd 1`

biggest square number smaller than the number of processors. It is clearly shown that using

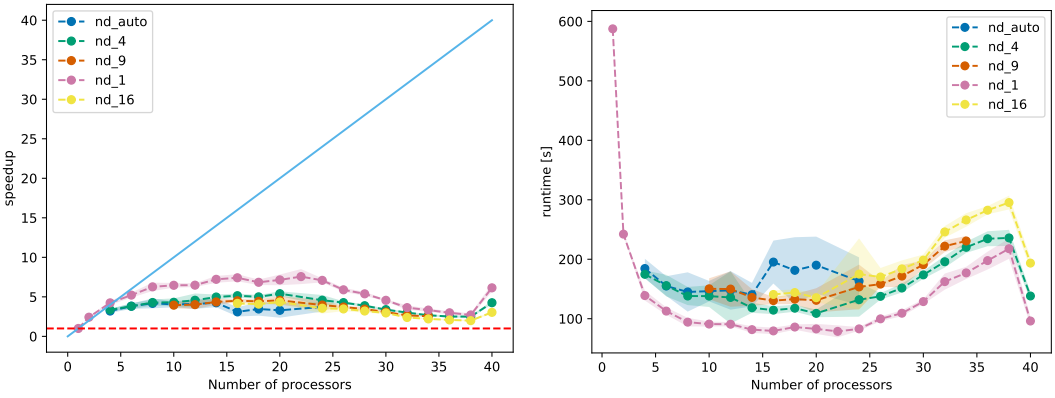


Figure III.13: *Scalability and runtime utilizing linear algebra parallelization for the Si benchmarking system,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nk 1`

linear algebra parallelization slows the calculation down significantly for the silicon system.

Interestingly, this again is not reproduced for the more expensive TaS_2 benchmarking system. Fig. **??** shows a pretty much consistent times across all values for `nd`.

Those results are already hinted at in the `PWscf` user guide [20]. Here, in the guide for choosing parallelization parameters, using linear algebra parallelization is recommended when the number of KS states is a few hundred or more. The silicon system has 8 electrons and is as such described with 4 KS states, the TaS_2 system has 153 electrons, so Quantum ESPRESSO uses 92 KS states (in case of metallic materials, the band occupation is smeared around the Fermi energy to avoid level crossings, so more KS states than $\frac{1}{2} *$ (number of electrons) are

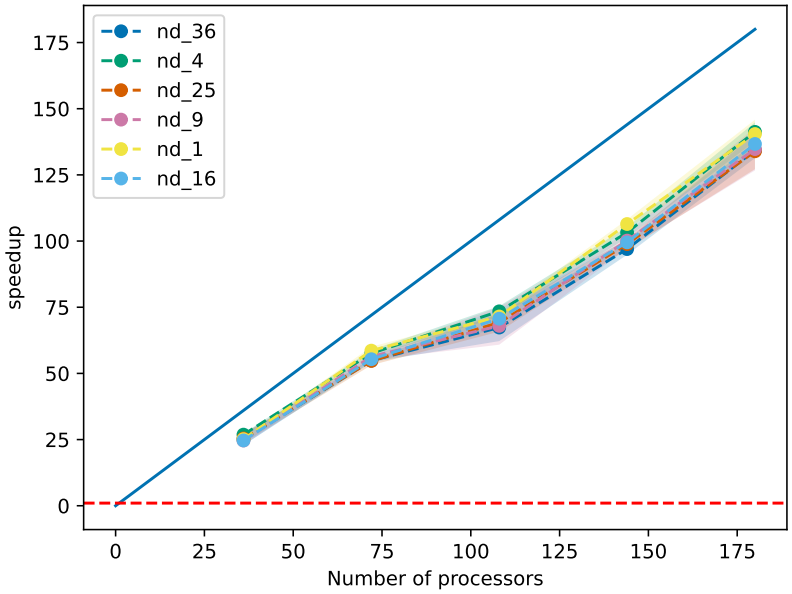


Figure III.14: *Scalability and runtime utilizing linear algebra parallelization for the TaS_2 benchmarking system,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nk` chosen such that pool size = 36

needed to account for that). Evidently, this number of KS states is on the edge of linear algebra parallelization actually speeding up calculations.

III.4 Comparison with calculations on the HLRN cluster

All calculations so far were exclusively run on the PHYSnet cluster and as such are limited by hardware and configuration present in the cluster. To assess this limitation, the k point benchmarks from sec. III.3.1 were run again on the another cluster, the HLRN cluster in particular. The North German Supercomputing Alliance (Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen - HLRN) operates a distributed supercomputer system at the Georg-August-Universität Göttingen and the Zuse Institute Berlin. The current iteration HLRN-IV has nodes with 2 Intel Cascade Lake Platinum 9242 CPUs (48 cores each) and an Omni-Path (Intels proprietary Infiniband competitor) connection between nodes. Quantum ESPRESSO is compiled with Intel Parallel Studio XE Composer Edition 2019 Update 5 (which is the predecessor of Intel oneAPI, bundled without MPI on the cluster) and Intel MPI 2018.5.

Fig. III.15 and III.16 show the benchmarks for the silicon benchmarking system.

The scaling behavior has some striking differences in comparison with the same benchmarks run on the PHYSnet cluster First of all, speedup and runtimes are very consistent across runs, with only a minimal variance across the whole range of processors. On a single node this is similar to the results from the benchmarks run on the PHYSnet, but on the HLRN cluster

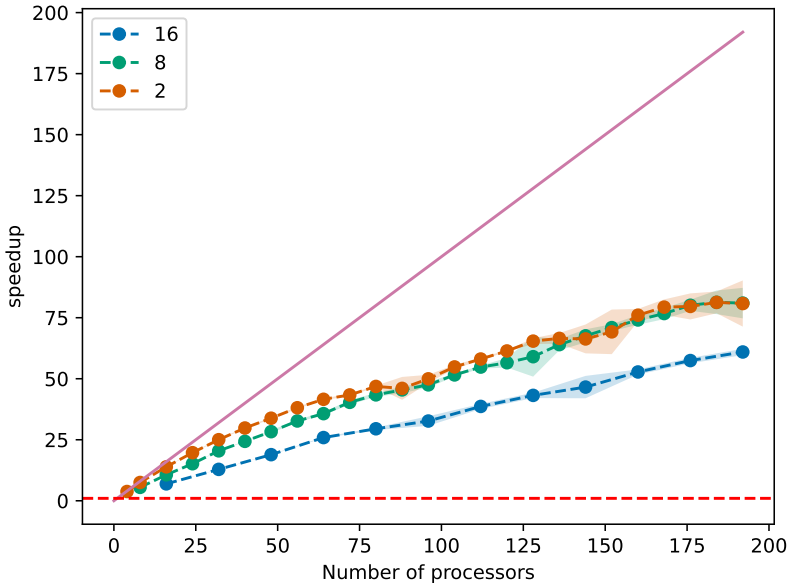


Figure III.15: *Scalability utilizing k-point parallelization for the Si benchmarking system with 3 different sizes of processor pools run on the HLRN cluster,* QUANTUM ESPRESSO compiled with Intel Parallel Studio 2019u5, Intel MPI 2018.5, `nd 1`

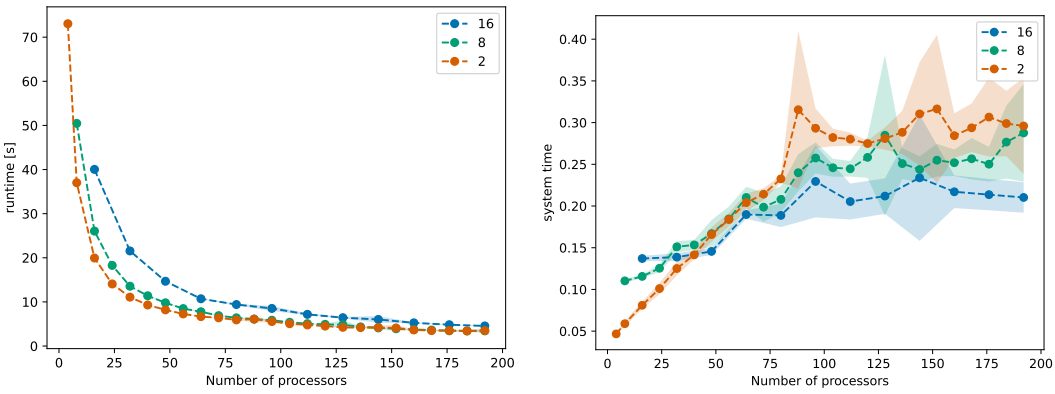


Figure III.16: *Absolute runtime and wait time for the scalability test with k-point parallelization for the Si benchmarking system run on the HLRN cluster,* QUANTUM ESPRESSO compiled with Intel Parallel Studio 2019u5, Intel MPI 2018.5, `nd 1`

this also holds true across two nodes (for more than 96 processors). This is most likely due to the HLRN cluster being equipped with better communication hardware, which is also the reason for the speedup further increasing over two nodes, whereas in the benchmark on the PHYSnet cluster, the maximum speedup of around 20 was already achieved for 24 processors.

A distinction between jobs running across on or two nodes can be made through the wait time though.

wait time and run time HLRN si

Another difference lies in the fact that the pool sizes 2 and 8 show a similar speedup with pool size 16 being a bit worse. This fact shows that while recommendations for parallelization parameters can be qualitatively made based on system size (more expensive system in terms of iterations, absolute runtime, etc. seem to benefit more from bigger k point pools, while smaller pools work best for smaller systems), the optimal size and processor range can vary depending on the compute cluster the calculations are run on.

Fig. III.17 and III.18 show the benchmarks for the TaS_2 benchmarking system. This benchmark was only run a single time, not averaged over multiple runs.

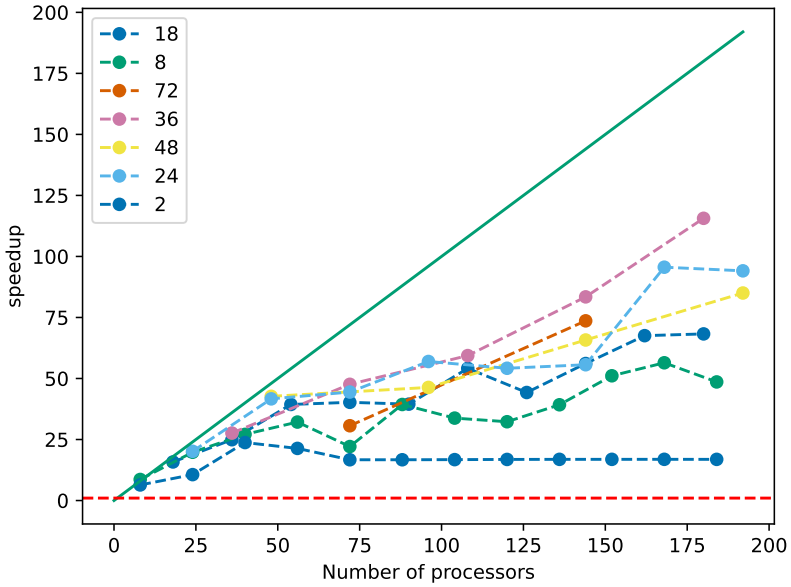


Figure III.17: *Scalability utilizing k-point parallelization for the TaS_2 benchmarking system over a range of processor pool sizes run on the HLRN cluster,* Quantum ESPRESSO compiled with Intel Parallel Studio 2019u5, Intel MPI 2018.5, `nd 1`

Interestingly, the upper bound for pool size is the same as for the calculations on the PHYSnet. In both cases, bigger pool sizes perform better up to 36 processors, with more processors per pool not showing better scaling. This suggests that this limit is not dependent on the compute cluster, but instead a property of the TaS_2 system: Just looking at the PHYSnet cluster, 36 as an upper limit might allude to an interpretation involving the size of nodes, where 36 processors is just under 2 full nodes and everything more will be spread over at least 3 nodes, with possibly more communication slowing down calculations. On the HLRN, the processor counts per CPU and node are different, so an analogous interpretation would suggest that the scaling gets better for pool sizes up to some multiple of 48 (the number of processors on one CPU). This is not the case, the processor pool of size 48 already shows worse scaling than the size 36.

This is an important result, as for the more expensive TaS_2 system the topology of the compute cluster seems to not be important for the scaling behavior. This opens up the possibility of using the PHYSnet not just for calculations but also for first finding the best parameters for a particular system (so just running a few iterations) and then doing the real calculation on a cluster like the HLRN.

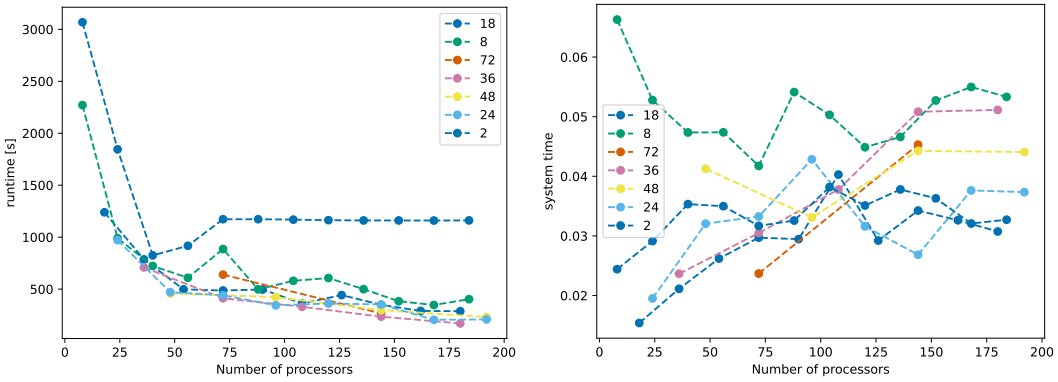


Figure III.18: *Absolute runtime and wait time for the scalability test with k-point parallelization for the TaS_2 benchmarking system run on the HLRN cluster,* Quantum ESPRESSO compiled with Intel Parallel Studio 2019u5, Intel MPI 2018.5, `nd 1`

analyse absolute times and wait times HLRN tas2

While the speedup plots look very similar between the PHYSnet and the HLRN, the absolute runtime in fig. III.18 shows a massive difference between the two clusters.

III.5 Conclusion: Parameters for optimal scaling

The benchmarks testing Quantum ESPRESSO's `PWscf` module showed that the speedup gained from parallelization of is highly dependent on the specific system. While calculations on the relatively inexpensive silicon benchmarking system gained performance just in a range up to 24 processors and were faster by a factor of 2, the more expensive TaS_2 benchmarking system benefitted more from parallelization itself and as such from all efforts improving parallelization.

Using the compilers and mathematical libraries from the Intel oneAPI package was shown to improve scalability beyond a single node, with the maximum speedup at around 32 processors for the TaS_2 benchmarking system. This value was then confirmed to be the best choice for the size of processor pools in k point parallelization not just on the PHYSnet cluster, but also on the more capable HLRN cluster.

A generalization for other systems beyond a qualitatively assessment that more expensive system profit more from parallelization than smaller system is not possible, but this chapter gives a guide on how to examine a system in order to get the optimal parameters.

IV Parallelization of DFPT calculations

The `PHonon` package enables calculations of phonon eigenvectors and eigenmodes. This chapter examines the best ways to run `PHonon` calculations.

IV.1 Optimal parallelization parameters for DFPT calculations

As discussed in sec. II.2.2, the `PHonon` package offers the same three parallelization levels as the `PWscf` package, namely plane wave, k point and linear algebra parallelization. Furthermore parallelization on q points (so called image parallelization) can be used.

IV.1.1 k point parallelization

In a first step, the same k point parallelization benchmark as in sec. III.3.1 is run. This is depicted in fig. IV.1.

Interestingly, the result from the `PWscf` calculation on silicon from sec. III.3.1 is not reproduced here: the smallest pool size of 2 is not the one parallelizing best, but instead it is pool size 8. Furthermore, for more than 50 processors, even the biggest pool size 18 shows better scaling than the pool size 2. This is similar to the results in the `PWscf` benchmark with k point parallelization on the TaS_2 benchmarking system in sec. III.3.1, as the separation between the different pool sizes isn't as clear as in the same benchmark on the silicon benchmarking system.

some more interpretation possible

The phonon benchmark has a similar runtime to the `PWscf` benchmark on TaS_2 shown in sec. III.3.1, so comparison in wait time can reveal differences in the quality of parallelization between the two systems. Whereas the `PWscf` benchmark on TaS_2 had wait time not exceeding about 8 % of the wall time, the wait time shown in fig. IV.2 between 10 % and 50 %. A possible explanation can be found how the time is actually spent during the calculation. In the case of the phonon calculation on silicon, the time of one iteration is on the scale of seconds, whereas one iteration for the `PWscf` calculation on TaS_2 is about 1 min.

some more interpretation

IV.1.2 Linear algebra parallelization

Fig. IV.3 shows that using linear algebra parallelization has so significant impact on the speedup, which is again in contrast to the results from sec. III.3.

a bit more interpretation should be possible

IV.1.3 Image parallelization

Better introduction

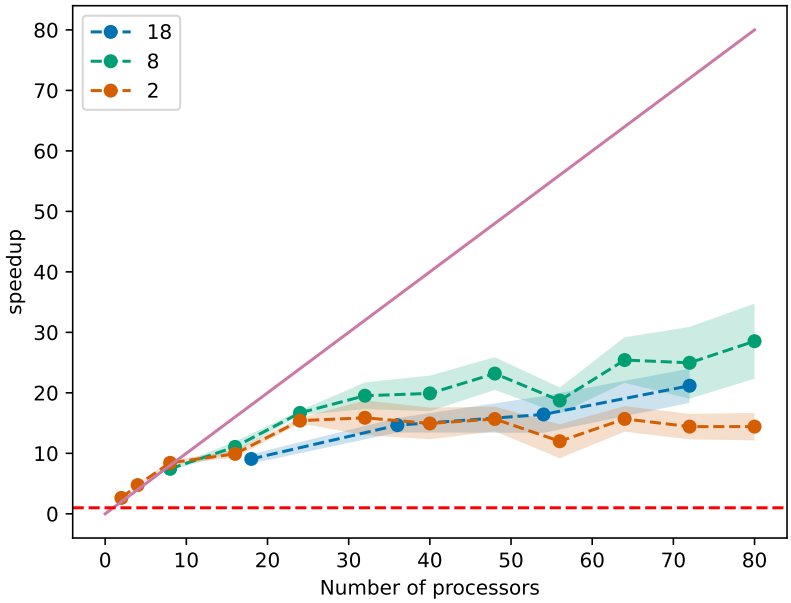


Figure IV.1: *Scalability utilizing k-point parallelization for the Si benchmarking system with three sizes of processor pools,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nd 1`

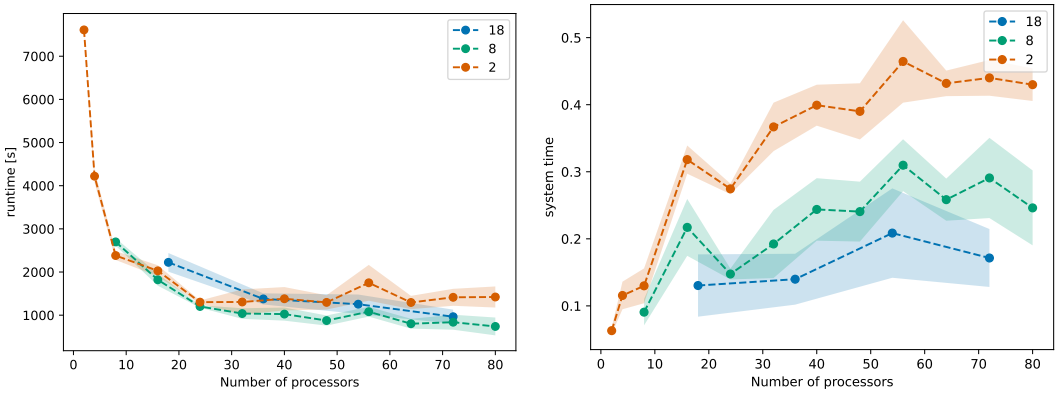


Figure IV.2: *Absolute runtime and wait time for the scalability test utilizing k-point parallelization for the Si benchmarking system with three sizes of processor pools,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nd 1`

When using image parallelization, Quantum ESPRESSO outputs a separate time report for every image, so one step is added to the analysis: The total runtime of a calculation is determined by the longest running image, so speedup will be calculated using that value, but another important measure to evaluate is variation of times between images. This is depicted in fig. IV.5.

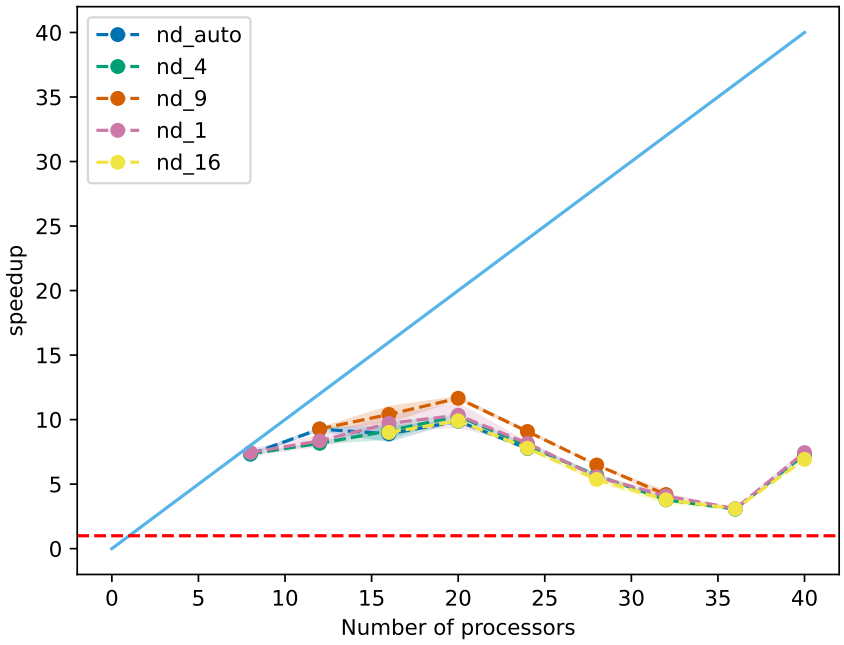


Figure IV.3: *Scalability utilizing linear algebra parallelization for the Si benchmarking system,* Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nk 1`

As the times between images don't vary much, good load balancing between images can be assumed for the silicon benchmarking system.

With the maximum time across images, speedup is then calculated, shown in fig. IV.5.

IV.2 Phonon calculations on TaS_2

The results from the last section can be used to estimate good parallelization parameters for a phonon calculation at the Γ point for TaS_2 in the charge density wave phase. The calculations were run on 180 processors, once with the previous established optimal pool size of 36 and once with a pool size of 18 for comparison. The relevant benchmark values for this calculation are listed in tab. IV.1.

Table IV.1: *CAPTION*

	runtime	wait time
pool size 18	3044 min	0.16
pool size 36	2020 min	0.074

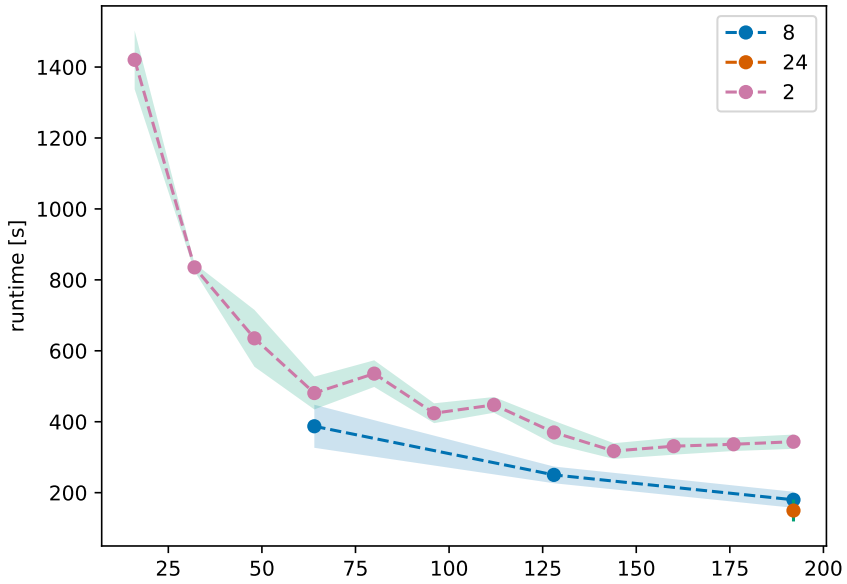


Figure IV.4: *Average runtime across images for the scalability test utilizing image and k point parallelization on the Si benchmarking system with three values of* `ni`, QUANTUM ESPRESSO compiled with Intel oneAPI 2021.4, `nk, ni` chosen such that poolsize = 8, `nd 1`

In this calculation the need for a good choice of parallelization parameters becomes especially clear: on the on the same number of processors, with the only difference in the choice of the parameter `nk`, the two calculations have a difference of 17 h.

IV.3 Conclusion: Parameters for optimal scaling

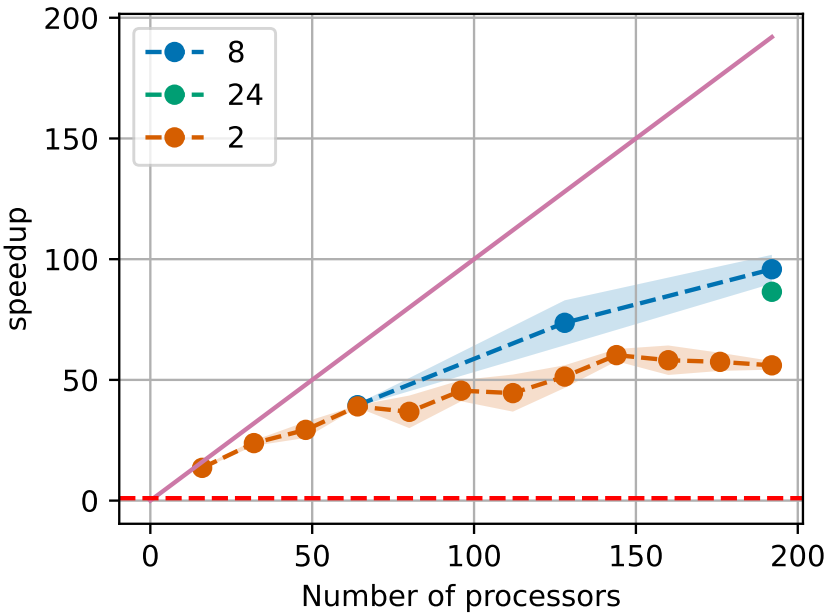


Figure IV.5: *Speedup calculated from the longest running image for the scalability test utilizing image and k point parallelization on the Si benchmarking system with three values of* `ni`, Quantum ESPRESSO compiled with Intel oneAPI 2021.4, `nk, ni` chosen such that poolsize = 8, `nd 1`

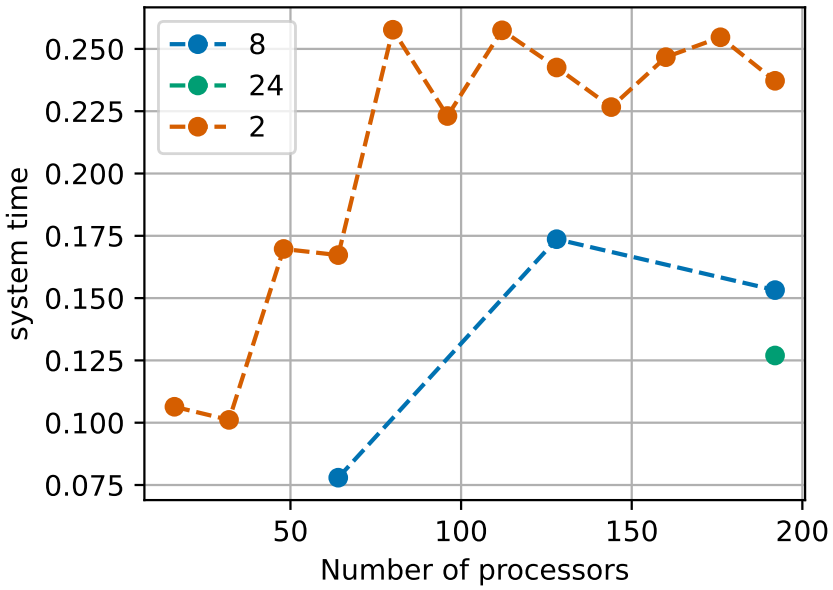


Figure IV.6: *Wait time calculated from the longest running image for the scalability test utilizing image and k point parallelization on the Si benchmarking system with three values of* `ni`, QUANTUM ESPRESSO compiled with Intel oneAPI 2021.4, `nk, ni` chosen such that poolsize = 8, `nd 1`

V Phonon mediated tunneling into TaS_2 (BETTER TITLE NEEDED)

V.1 Amplitude mode in TaS_2

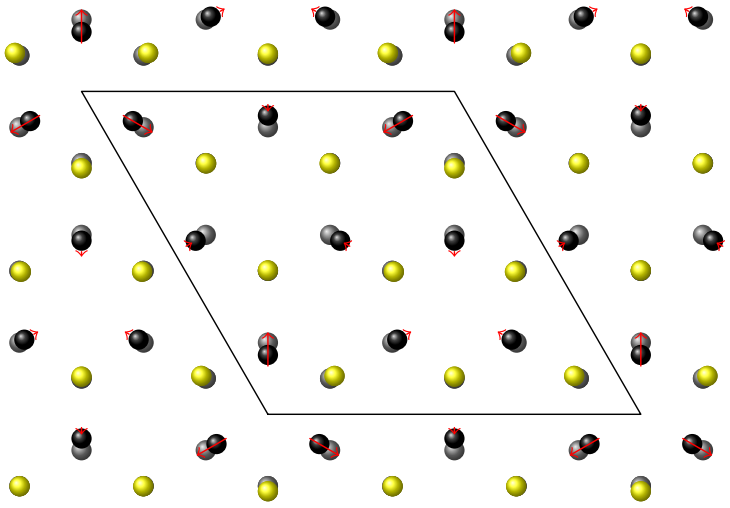


Figure V.1

V.2 Scanning Tunneling Spectroscopy

Scanning Tunneling Spectroscopy (STS) is an experimental technique in which a Scanning Tunneling Microscope (STM) is used to map the density of states of a material.

introduction stm/sts

Stipe et al. noted that the tunneling current in STS can also identify phonon modes of the material measured [25] (vibrational modes of a single molecule in this case).

V.3 Phonon mediated tunneling in Graphene

A gap feature around the fermi level in the measured DOS on graphene [26] was explained with electron-phonon interaction [27].

Graphic for that would be nice

The underlying mechanism is that electrons can elastically tunnel into graphene at the Fermi level near the **K** point. This elastic process is suppressed because the wave function at the initial state i.e. the wave functions at the tip have a momentum distribution centered at $\boldsymbol{k}_{\parallel} = 0$, so the tunneling matrix element is suppressed for large $\boldsymbol{k}$ [28]. For electron energies larger than the energy

V.4 Phonon mediated tunneling into TaS_2

In a 2019 paper by Hall et al. [6], a similar gap feature with a width of $2\Delta = (32 \pm 9)\,\mathrm{meV}$ was recorded in an STS measurement on TaS_2.

explain cdw phase, gap due to peierls somewhere, reference here

This gap is attributed to partial gapping to the formation of the charge density wave.

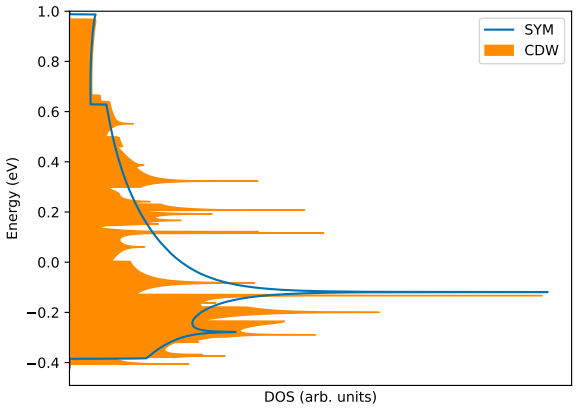


Figure V.2: *Density of states for TaS_2 in the charge density wave (CDW) and undistorted (SYM) phase. The data was kindly provided by Dr. Jan Berges and has been calculated using the 2D tetrahedron method using 360^2 (1080^2) k points for the CDW (SYM) structure*

woher kommt die genau? Quantum Espresso?

The density of states shown in fig. **??** shows no symmetric gap around the Fermi level.

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