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Increasing the QUANTUM ESPRESSO Capabilities II: Towards the TDDFT Simulation of Metallic Nanoparticles

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Abstract

This work regards the enabling of the Time-Dependent Density Functional Theory kernel (TurboTDDFT) of Quantum-ESPRESSO package on petascale systems. TurboTDDFT is a fundamental tool to investigate nanostructured materials and nanoclusters, whose optical properties are determined by their electronic excited states. Enabling of TurboTDDFT on petascale system will open up the possibility to compute optical properties for large systems relevant for technological applications. Plasmonic excitations in particular are important for a large range of applications from biological sensing, over energy conversion to subwavelength waveguides. The goal of the present project was the implementation of novel strategies for reducing the memory requirements and improving the weak scalability of the TurboTDDFT code, aiming at obtaining an important improvement of the code capabilities and to be able to study the plasmonic properties of metal nanoparticle (Ag, Au) and their dependence on the size of the system under test.

The Scientific Challenge

The optical properties of nanostructured materials and nanoclusters are determined by their electronically excited states. In particular, plasmonic excitations are particularly relevant for a large range of applications such as biological sensing, energy conversion and subwavelength waveguides [1-4]. In solid-state physics the electronic excitations are classified as single-particle excitations and plasmons. The distinction of plasmons and single-particle excitations can be motivated from the homogeneous electron gas model. Plasmons in extended systems are usually well-described by classical electrodynamics (e.g. Drude-Lorentz model) [5]. For molecules and nanoparticles classical models are no longer applicable and a full quantum-mechanical treatment is necessary [6,7]. In this case, the optical spectrum does not show a single strong plasmon feature, but instead a spectrum with distinct peaks due to transitions between discrete energy levels, typical of a finite system. When increasing the size, the optical spectrum curve obtained from full quantum-chemical calculations is expected to approach the single plasmon feature of the one predicted by classical models.

Density-functional theory (DFT) is considered the state of the art in the molecular modelling of materials at the atomic (nano) scale, allowing one to simulate models consisting of several hundred up to a few thousand atoms. The situation is not nearly as favourable for those spectroscopies, such as optical and UV absorption, which probe electronic excitations. Time-dependent (TD) DFT is emerging as alternative route to extend the scope of DFT to dynamical processes [8]. However, its numerical complexity has long been considered a restricting bottleneck, resulting in a substantial (one to two orders of magnitude) reduction of the size of systems that could be addressed. Thus, so far the standard realm of TDDFT was the study of small (tens to hundred atoms) molecules or clusters.

Recent algorithmic advances based on Liouville-Lanczos approach to TDDFT [9-10] partially overcome these hurdles and allow to model the optical activity of systems of unprecedented size, such as large (bio)molecules and metallic nanoparticles. This new methodology –implemented in the TurboTDDFT code, included in the Quantum-Espresso package [11]– allows one to compute the absorption spectra of complex molecular and nanostructured systems, using a numerical workload that, for an entire wide energy range, is comparable (only a few times larger) than that needed for a standard ground-state (or static response) calculation in a same system. Nonetheless the simulation of realistic "plasmonic" systems (both nanoparticles and molecules) with hundreds to thousand atoms is still a computational challenge.

TurboTDDFT and Quantum Espresso package

Quantum Espresso (QE) is a suite of inter-operable codes with two main kernels: pwscf, for total energy ground state simulations; and cp, for Car-Parrinello like simulations. All other kernels are designed for computation of ground state properties, post-process like analysis or correction to the DFT approximations for more accurate results. TurboTDDFT is one of these kernels, mainly meant to compute optical properties. It requires, as a pre-process step, a pwscf simulation for the structural and electronic ground state.

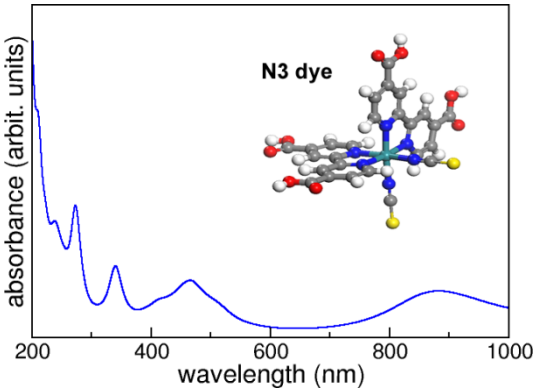
The fact that QE is a suite of codes, implies strengths and weaknesses. Strengths are the fast and modular development of core components that allow the package to run and scale on every HPC systems present in the market; on the other hand among the weaknesses not all kernels are at the same level of development, especially in term of adoption of new programming paradigms. Usually new parallelization paradigms are first introduced and validated in cp and pwscf main kernels and then ported to other kernels. Following this scheme, in the present work we have implemented in TurboTDDFT a parallelization technique already validated in cp and pwscf, named "task grouping". Task grouping was first implemented in cp kernel code [12] to exploit the extreme parallelism of BlueGene architecture, and then ported on pwscf.

Task group is a key technique to allow the 3D parallel FFT implemented in plane wave DFT codes like QE or CPMD, to scale beyond the number of "planes" in the z direction of the domain. Due to the specific characteristic of the reciprocal basis set (determined by the kinetic energy cut-off) the 3D FFT it is parallelized by scattering z columns (all points in the domain having the same values for x and y coordinate) in reciprocal space, and distributing the z "planes" (all point having the same value for z) in real space. Task group, as the name says, groups together many electronic bands (each one requiring a forward and backward 3D FFT) to be processed at the same time, and allowing for a greater scalability. The groups are implemented using communicators. With this implementation the new limit to the scalability is given by the number of z "planes" multiplied by the number of task group.

Test Cases

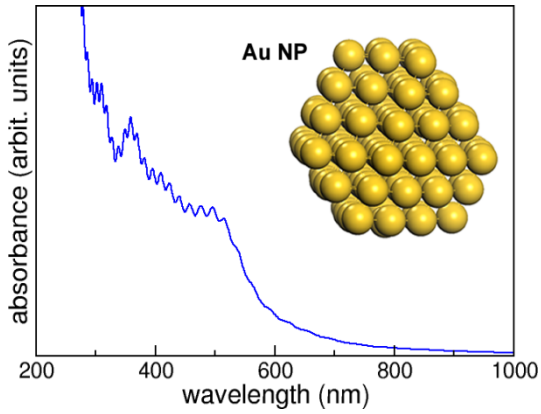
In this project we considered two representative systems: one Ru-based molecular dye (namely N3) and one Au nanoparticle, which have the same order of magnitude in terms of number of atoms but a very different number of electrons. The latter is the most critical parameter for the performances of the TDDFT code, since it is responsible for the electron-hole transitions of the optical spectrum. For each system, we first calculated the electronic structure groundstate by using the DFT code (pwscf) included in QE, then we run the TurboTDDFT code for the evaluation of the optical spectra. The promising results obtained after the improvement of the code, e.g. the reduced CPU time and memory required also in the case of the Au nanoparticle (see below), pave the way for the simulation of nanometer scale nanoparticles to be directly compared with the experimental ones.

Test 1. Molecular system: N3 dye [bis-(2,2'-bipyridine-4,4'-dicarboxylate)-Ru(II)].



Numerical details: Number of atoms = 59, number of electrons= 218, cell=(19.0x19.0x19.0)Å^3, Ecut=25Ry, FFT=(192x192x192), XC=PBE, USPP..

Test 2. Gold nanoparticle.



Numerical details: Number of atoms = 92, number of electrons= 1012, cell=(25.0x25.0x25.0)Å^3, Ecut=25Ry, XC=PBE, USPP, FFT=(216x216x216)

Performances

We are mainly interested within this project in the weak scalability on real dataset, allowing to run large system with lots of electrons. Test1 and Test2 have been chosen as a meaningful (scientifically speaking) production data set, of different size. Test1 involves 59 atoms, 109 electronic bands and 98385 basis vectors. Test2 involves 92 atoms, 506 electronic bands and 219223 basis vector. The number of atoms plays a minor role in determining the size and the wall time, which instead depend strongly from the number of electronic bands and the number of basis vectors. Moreover, the complexity of the algorithm do not scale linearly with the number of basis vectors and number of bands (but superlinear), then we have only a rough estimate of the weak scalability. If we neglect this non-linearity of the algorithm for the purpose of the present benchmark, we observe that Test2 is 10.2 time larger than Test1, see **Table 1**.

Table 1: result of the scaling benchmark.

Test case name	Test case size	Number of core	Wall time	size / size Test1	cpu hours / Test1 cpu hours
Test1	98385 * 109	1024	43 min	1	1
Test2	219223 * 506	2048	296 min	10.2	13.7

As can be seen from **Table 1**, the computational resources required by the large test case Test2 is 13.7 times larger than the computational resources required by Test1. Test2 being 10.2 times larger than Test1, and considering that the algorithm complexity is superlinear, we can conclude that the TurboTDDFT code with new task group parallelization scale fairly well with real case datasets.

Hermit specific issues

Several test runs have been performed (using cp kernel and W256, 256 water molecule, dataset) to find out the best combination of compilers, libraries and execution environment. As the compiler we used Intel suite (through the ftn Cray wrapper) with an optimization level O2 (in QE performances mainly depends on libraries); as the library for linear algebra we used Cray scilib, for the FFT we used a custom 3D FFT linked with FFTW (version 2.5). But the most important issues we discover about the performance on Hermit, is related to the task/thread affinity (QE perform and scale best with a combination of 4 to 8 threads per tasks). To make the code perform at best we need to explicitly specify "-cc numa_node" on the aprun command line. In **Table 2** we report the performance registered for two run with and without the "-cc numa_node" flag.

Table 2: Performance of the cp kernel with W256 dataset. 2048 cores, 512 tasks, 4 threads per task.

Launch command	Recorded time
aprun -n 512 -N 8 -d 4 ./cp.x -ntg 4 -nbgrp 2 -input cp.in > h2o.out.test.11 2>&1	4m19.80s CPU 6m 0.14s WALL
aprun -n 512 -N 8 -d 4 -cc numa_node ./cp.x -ntg 4 -nbgrp 2 -input cp.in > h2o.out.test.11 2>&1	7m54.39s CPU 2m13.18s WALL

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Acknowledgements

This work was financially supported by the PRACE-2IP and -3IP project funded in part by the EUs 7th Framework Programme (FP7/2007-2013) under grant agreement no. RI-283493, RI-312763.