JOINT INSTITUTE FOR NUCLEAR RESEARCH
Bogoliubov Laboratory of Theoretical Physics

FINAL REPORT ON START PROGRAMME

Theoretical study of the electronic properties of carbon nanostructures.

Supervisor:
Dr. Vsevolod Katkov

Student:
Jorge Joe Espinosa Ventura
Center for Advanced Studies of Cuba (CEA)

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Abstract

The temperature dependence of the band gap $E_g(T)$ is one of the fundamental signatures of a semiconductor, providing important insight into the nature and strength of electron-phonon (e-p) interactions. This dependence on the carbon quantum dot would be important by the weight that this represents in explaining the fluorescence and the searching of the new applications and applications and dependencies on determined optical measurements. In this study, we employed the "frozen-phonon" method because, as demonstrated by previous calculations, it provides the same results for carbon nanotubes **(CNTs)** as the special displacement method but with reduced computational effort. This method, along with its modifications (in combination with the GW approximation and the Monte Carlo method), has been applied to calculate the renormalization of the band gap in various semiconductors.

1 Introduction

Nanosized carbon-based materials, such as fullerenes, nanotubes, graphene, and quantum dots, have attracted the attention of scientists due to their unique physicochemical characteristics, often very different from those of the original bulk material. The nanotubes of Carbon in particular are hollow cylinders of graphite sheets Prof. C. Thomsen (2004). They can be looked at as single molecules, regarding their small size ($\sim nm$ in diameter and $\sim \mu m$ length), or as quasi-one dimensional crystals with translational periodicity along the tube axis. They also have semiconductor properties in which the temperature dependence of the band gap $E_g(T)$ is one of the fundamental signatures due to the importance of the control of the gap of the material. In the same way, providing important insight into the nature and strength of electron-phonon (e-p) interactions.

The ability to measure the optical gap in individual single-walled carbon nanotubes (SWNT), combined with data from vibrational spectroscopy, provides a pathway for the assignment (n, m) of SWNT. This assignment determines the specific chirality of the nanotube. Comprehending the temperature dependence of $E_g(T)$ for nanotubes is critical in this context. This is because experimental measurements are typically conducted at room temperature, while (n, m) assignments often rely on comparing observed optical transition patterns with theoretical predictions calculated at $T = 0K$. This discrepancy in temperature can introduce significant errors in the assignment.

This report focuses on obtaining the accurate geometry of a (10,0) carbon nanotube and comparing various DFTB+ parameterizations. The goal is to identify parametrization that can reliably reproduce the results from tight-binding and molecular dynamics simulations. The study will also investigate the temperature dependence of the band gap for the CNTs.

2 Calculation Method

Determining the temperature dependence of the band gap, $E_g(T)$, is complex due to the various approximations involved. This dependence on constant pressure involves two-term harmonic and anharmonic contributions, $(\frac{\partial E_g}{\partial T})_P = (\frac{\partial E_g}{\partial T})_{har} + (\frac{\partial E_g}{\partial T})_{anh}$ Capaz u. a. (2005). Still, the anharmonic term is due to thermal expansion. The harmonic term is the most difficult determinate and has been terminated by several methods and arises from the e-p interaction evaluated at ground state geometry Allen und Heine (1976), Fan (1951), Allen und Cardona (1981). An efficient method based on the special displacement approach has recently been employed to calculate the $E_g(T)$ dependence for different graphene quantum dots Zacharias und Kelires (2021). This method, along with its modifications (in combination with the GW approximation and the Monte Carlo method), has been applied to calculate the renormalization of the band gap in various semiconductors Zacharias und Giustino (2016). This approach can be seen as an extension of the thermal line and "frozen-phonon" methods Lam und Cohen (1982).

It was used to study the temperature dependence of carbon nanotube band gaps within the tight-binding method; the computation is based on the change of eigenergies due to atomic displacement followed by a Bose-Einstein weighted sum (statistic average) of the contribution of each mode. It means direct evaluation of electron-phonon coupling within a "frozen-phonon" schema.

Initially obtained for a correct supercell (correctly optimized) the spectrum of the phonon modes (ω_i) and the corresponding set of polarization vectors $\boldsymbol{\varepsilon}_i$, normalized in a conventional way $\boldsymbol{\varepsilon}_i \boldsymbol{\varepsilon}_j = \delta_{ij}$.

Then, with the shift of an electronic eigenergies $\Delta E_{n,k}$ of band n and wave vector k and the static displacement from equilibrium around the second-order Taylor expansion:

$$\Delta E_{n,m} = \mathbf{u} \cdot \nabla E_{n,k} + \frac{1}{2} \mathbf{u} \cdot \mathbf{D} \cdot \mathbf{u}, \tag{1}$$

where $\mathbf{u}$ is a 3N-coordinate displacement vector and $\mathbf{D}$ is the corresponding $(3N \times 3N)$ Hessian matrix (N is the corresponding number of atoms) $\mathbf{u}$ the displacement the expresses as:

$$u(\alpha, \kappa) = \sum_j \left(\frac{\hbar}{2 M_\kappa \omega_j} \right)^{1/2} \varepsilon_j(\alpha, \kappa)(a_j^\dagger + a_j), \tag{2}$$

where $u(\alpha, \kappa)$ is the displacement along the direction α of the atom κ in the unit cell with mass M_κ and it is determined by the frozen-phonon displacement $\mathbf{x}$. The $a_j^\dagger, a_j$ are creation and annihilation operators for phonons, and $\varepsilon_j(\alpha, \kappa)$ are components of the properly normalized polarization vectors. If substitute Eq. (2) into Eq. (1) and perform a thermal average are obtained:

$$\Delta E_{n,\kappa} = \sum_j \frac{\partial E_{n,k}}{\partial n_j} (n_j + 1/2), \tag{3}$$

where $n_j = (\exp(\beta \hbar \omega_j) - 1)^{-1}$ is the Bose-Einstein occupation number of the phonon mode j and the e-p coupling coefficient $\partial E_{n,k} / \partial n_j$ is given by:

$$\frac{\partial E_{n,k}}{\partial n_j} = \frac{1}{2} \mathbf{x}_j \cdot \mathbf{D} \cdot \mathbf{x}_j, \tag{4}$$

where $\mathbf{x}_j(\alpha,\kappa) = (\frac{\hbar}{M_\kappa \omega_j})^{1/2} \boldsymbol{\varepsilon}_j(\alpha,\kappa)$ are the displacement of the frozen-phonon. In practice, $\partial E_{n,k}/\partial n_j$ is calculated by performing electronic structure calculations for $\pm\mathbf{x}_j$ and averaging the obtained energy shifts to eliminate the linear term.

The structure optimization and calculation of phonon modes were conducted using the DFTB+ van der Heide u. a. (2024) program package, which includes the MODES software Hourahine u. a. (2020). The tight-binding integral parametrization method GFN1–xTB Grimme u. a. (2017) was utilized as it produces phonon spectra for pure CNTs that closely match those obtained with the DFT method. To achieve the desired accuracy in calculating the energy level positions, we employed the hopping parameter matrices **H** and the corresponding wavefunction overlap matrices **S** derived from DFTB+, following a similar approach.

3 Results and Discourses

3.1 Optimizations

In the initial instance, the correct parameters and the correct geometry (see Figure 1) were used for the chirality (10,0) carbon nanotube with a supercell of (1×1×5), containing $2 \cdot 10^2$ atoms.

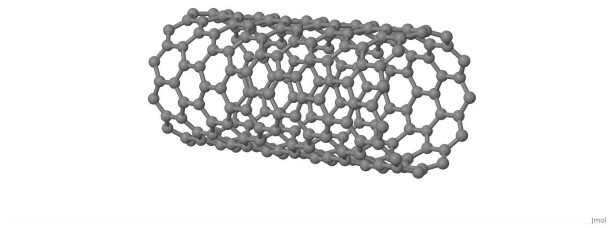
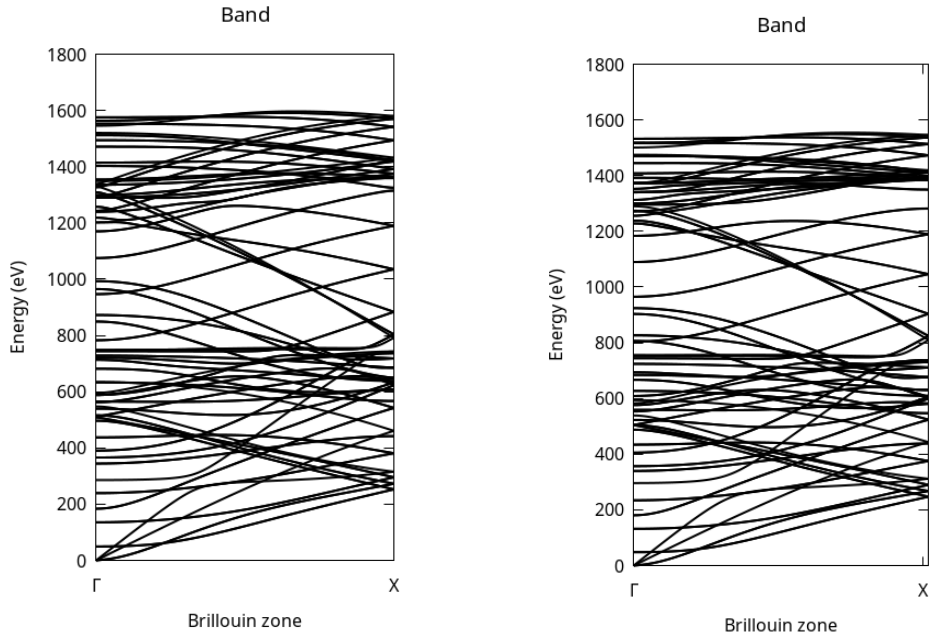


Figure 1: The previous figure was represented the optimizer geometry for the nanotube of configuration (10,0).

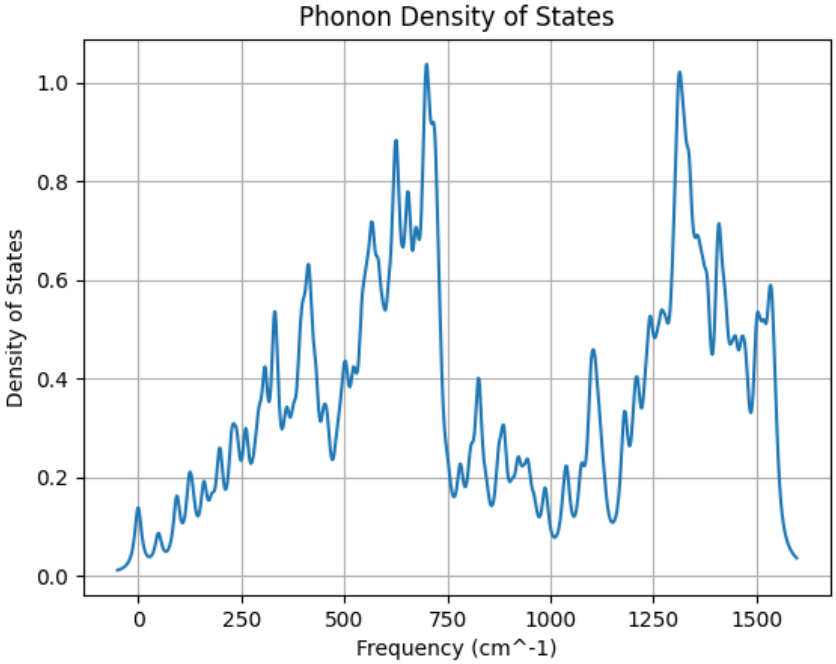
The correct prediction of the band structure was obtained by comparison with ab initio calculations from Dubay und Kresse (2003), using different parametrizations, including ob3-frequencies Gaus u. a. (2013), matsci Lukose u. a. (2010), x-TB Hourahine u. a. (2020), pbc Köhler und Frauenheim (2006), and mio Elstner u. a. (1998). The relationship between ob3-frequencies and x-TB was found to accurately predict the dispersion relations shown in Figure 3, as well as the vibrational density of states depicted in Figures 2a and 2b. Later, Phonopy Togo u. a. (2023) was employed to obtain new frequencies and densities of state (Figure 6) for comparison. These results were compared with those from Dubay und Kresse (2003), confirming DFTB+ van der Heide u. a. (2024) as an efficient computational method.



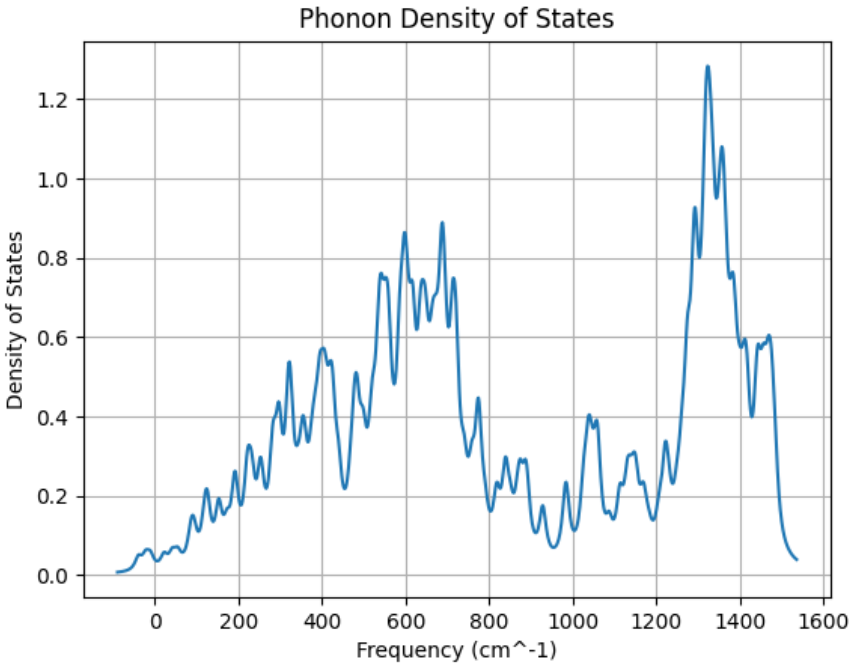
(a) Phonon band structure for ob3-frequencies parametrization

(b) Phonon band structure for x-TB parametrization

Figure 2: Phonon band structure for different DFTB+ parametrizations represented in the first Brillouin zone



(a) Phonon density of state for ob3-frequencies parametrization



(b) Phonon density of state for x-TB parametrization

Figure 3: Phonon density of state for different DFTB+ parametrizations represented in the first Brillouin zone.

3.2 Temperature dependence of the Band Gap

To calculate the temperature dependence on the gap we used only x-TB parametrizations. In the figure 4 we can say that dependence is relatively small and has good approximation by obtained in Capaz u. a. (2005).

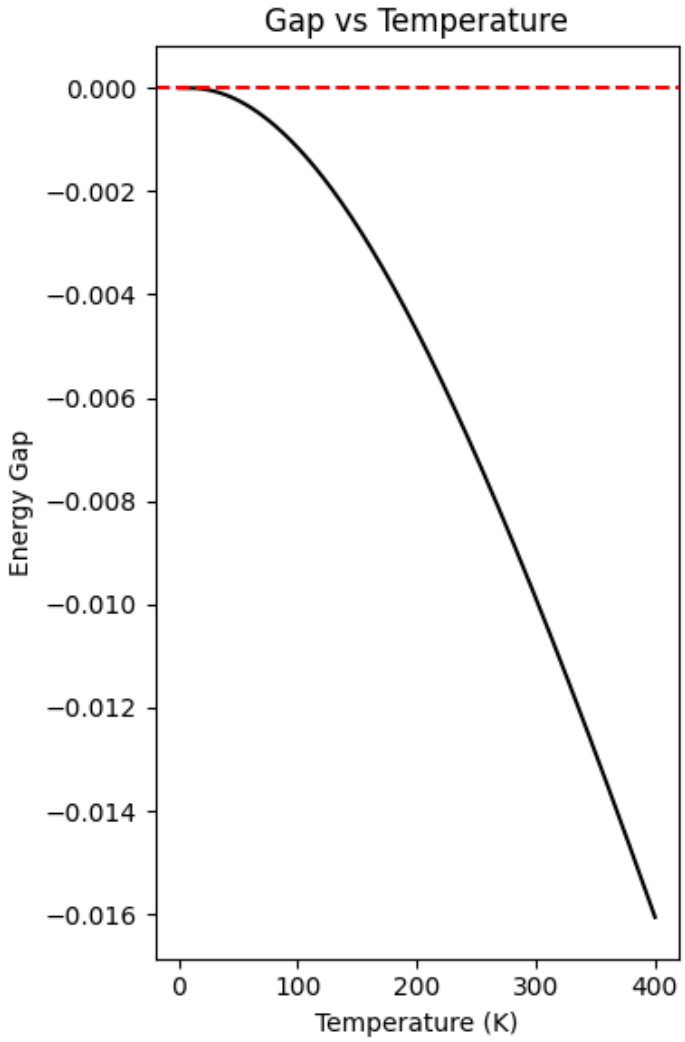


Figure 4: It was representing the temperature dependencies of the Band gap

Now it will analyze the contributions to $E_g(T)$ from the different phonon modes. This information is contained in the e-p spectral function for the gap, g^2F, defined as:

$$g^2F(\Omega) = \sum_j \frac{\partial E_g}{\partial n_j}\delta(\Omega - \omega_j). \tag{5}$$

Note that $\partial E_g/\partial n_j$, defined as the difference between coupling coefficients for the two band-edge states, can be positive or negative. The plot (figure 4) is restricted to the low-energy phonon branches, the relevant ones to describe $E_g(T)$ for $T < 400K$. We notice the g^2F (solid black line) is highly structured, reflecting the complexity of the phonon dispersion of this material, even at low energies. At the same time was established that the low energy optical "shape deformation" modes (SDM) near provide the most important contributions to g^2F at low energies such as in Capaz u. a. (2005). This family of modes is derived, in a zone-folding scheme, from the out-of-plane transverse acoustical

(ZA) branch of graphene and they deform the circular cross-section of the tubes into a sequence of shapes: ellipse (the so-called "squashing mode"), triangle, square, pentagon, etc corresponding to each minimum of figure 5. For the (10,0) tube, the contribution to g^2F from these modes is strongly negative and dominates the full g^2F up to phonon energies equivalent to 500 K.

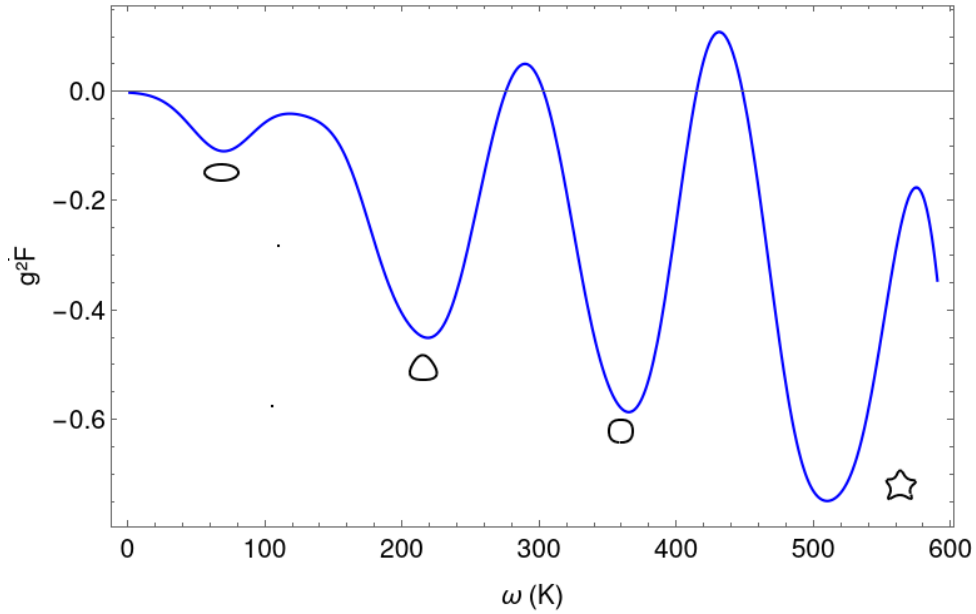
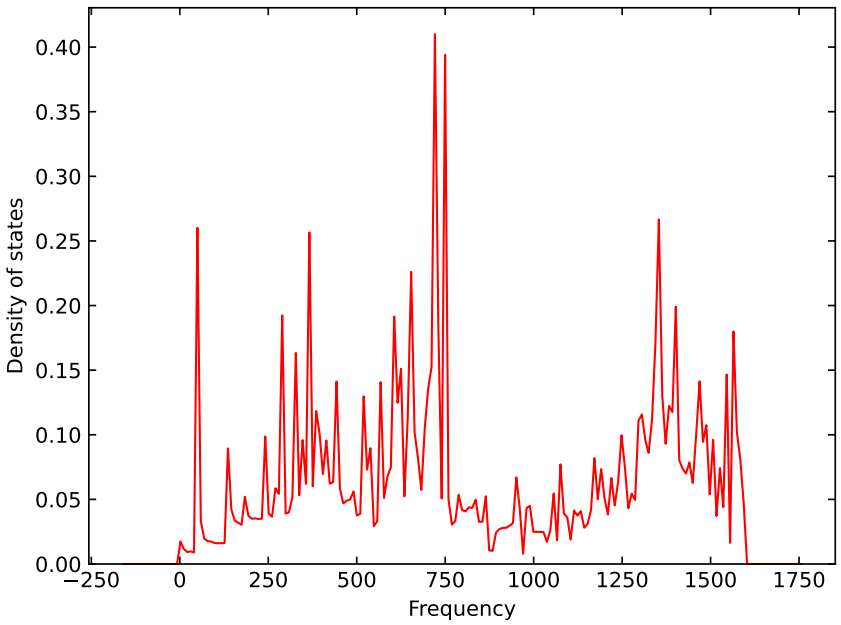
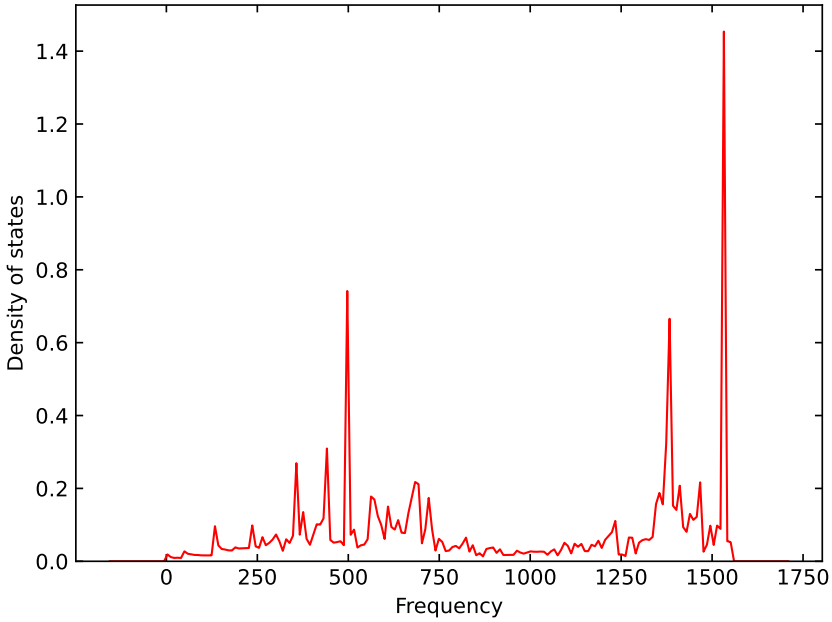


Figure 5: It was represented by the contributions to $E_g(T)$ from the different phonon modes.



(a) Phonon density of state obtained on phonopy for ob3-frequencies parametrization



(b) Phonon density of state obtained on phonopy for x-TB parametrization

Figure 6: Phonon density of state obtained with phonopy for different DFTB+ parametrizations represented in the first Brillouin zone.

4 Conclusion

The frozen-phonon is a well-established method for calculating the temperature-dependent band gap. Its implementation within the DFTB+ framework yields promising results when compared to molecular dynamic calculations. Moreover, the ob3-frequencies and x-TB parametrizations exhibit high accuracy in predicting the band structure of carbon nanostructures. This work lays the foundation for applying DFTB+ in calculating the temperature-dependent of band gap of more complex carbon nanostructures, such as amorphous carbon quantum dots. This advancement would enable a deeper understanding of these nanostructures and opening-up new avenues for their applications.

5 Acknowledge

I am usually a man of few words, but I value deeply and like acknowledging good intentions in people. First and foremost, I thank Guzmán for being the person who has trusted in me and my intellect. Though my mind sometimes gets clouded, he always helps me find clarity. To my supervisor Katkov, thank you for your dedication and for teaching me with such clarity. I leave with the joy of having met you and with the enthusiasm to continue working with you from afar. I hope and wish that you become a great friend. I would like to express my gratitude to the Russian people in general and for the friendships I have made in these two months. They leave with my heart warm and my soul fulfilled.

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