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Linear and Non Linear Optical Responses in terms of Density Functional Theory

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ABSTRACT

This paper analyzes the linear and non linear optical responses in terms of density functional theory. Nonlinear optical materials play a crucial role in the future evolution of nonlinear optics and its impact in technology and industrial applications are excellent. Nowadays the time dependent range separated density functional theory is the most popular method for ground state electronic structure calculations in quantum chemistry, non-linear optical materials and solid state physics. When compared to traditional and semi-empirical approaches the contemporary density functional methods show a favorable balance between accuracy and computational efficiency.

Keywords: nonlinear, optics, optical, response, DFT, density, theory.

INTRODUCTION

The interest in density-functional theory has increased steadily since Hohenberg et. al provided its theoretical justification and Kohn et. al its practical formulation for calculations. The independent-particle Kohn– Sham model, which describes correlation in terms of a unique, albeit unknown, functional of the electron density, has had an enormous impact on computational chemistry, and the available approximate exchange-correlation functionals have provided a level of accuracy that is adequate in many situations. The generalization of the Kohn–Sham equations by Runge and Gross represents an important milestone in the development of time-dependent DFT (TDDFT). Thus, although most applications of DFT have focused on structure and static properties, the interest in time-dependent response properties has grown considerably in recent years. At the same time one has witnessed a great success of ab initio wave function quantum chemistry in computing molecular properties for nonvariational and variational wave functions using time-independent analytic gradient theory and time dependent response theory.

Recently, time-dependent properties have been obtained also from the quasienergy ansatz, where properties of any type (linear, nonlinear, static, dynamic, magnetic, electric, internal, external) are obtained from the solution of a common set of equations, without further parametrizations or manipulations than those applied to the reference wave function. Considering the broad range of systems that nowadays can be treated at an acceptable level of accuracy by DFT, the implementation of such a ‘‘toolbox approach’’ for DFT calculations of molecular properties would have broad ramifications. An implementation should then involve all the common forms of the exchange correlation functional, also those that include some proportion of the Hartree–Fock exchange. When the electron density is calculated as an expectation value of the density operator, all the changes in the density to a given order in the perturbation are obtained as the terms of a Baker– Campbell–Hausdorff expansion.

Within the framework of Kohn–Sham DFT (KS DFT), the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the local-density approximation (LDA), which is based upon exact exchange energy for a uniform electron gas, which can be obtained from the Thomas–Fermi model, and from fits to the correlation energy for a uniform electron gas. Non-interacting systems are relatively easy to solve as the wave function can be represented as a Slater determinant of orbitals. Further, the kinetic energy functional of such a system is known exactly. The exchange-correlation part of the total-energy functional remains unknown and must be approximated.

Another approach, less popular than KS DFT but arguably more closely related to the spirit of the original H-K theorems, is orbital-free density functional theory (OFDFT), in which approximate functional are also used for the kinetic energy of the non-interacting system.

RELATED WORK

The design of efficient organic materials for applications in nonlinear optical effect is based on asymmetric polarization, induced by electron donor and electron acceptor groups on either side of the molecule at appropriate positions in the molecular systems. Due to their commercial importance in the fields of optical communication, signal processing, sensing and instrumentation, nonlinear optical materials capable of producing second harmonic generation, have been studied [2-3].

In order to understand the microscopic origin of nonlinear behavior of organic NLO materials, considerable theoretical and experimental investigations have also been made [5].

These efforts have brought its fruits in applied aspects of nonlinear optics. To obtain information on the behavior of normal modes, the effect of various types of intermolecular forces and the nature of hydrogen bonding on these nonlinear optical materials, IR and Raman spectroscopy has been used. Information about electronic transitions can be achieved by the analysis of UV-visible spectrum [6-8].

Since atoms or molecules absorb UV-visible radiation at different wavelength, spectroscopy is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.

For the computation of molecular structure, vibrational wavenumbers and energies of molecules, ab initio community has accepted Density functional theory (DFT) study as a popular post-HF (Hartree Fock) approach [6] because of its efficiency and accuracy with respect to the evaluation of a number of molecular properties. DFT calculations are also useful for gaining insight into the nonlinear optical properties of conjugated molecules. In a series of recently performed overlay calculations, a force field for some conjugated molecules has been constructed [8] and full normal coordinate analysis has been performed by means of the MOLVIB program written by T. Sundius [9].

This includes transformation of the DFT force field to natural internal coordinates and scaling of the quadratic force field according to Pulay's method [44,45] by a set of scale factors refined in a least-square procedure which helps to achieve better agreement between the calculated and observed frequencies. In the cinnamic acid molecule, the carboxylic group is separated from the aromatic ring by a double bond. It causes conjugation between the –C=C–bond and the π-electron system. In order to study the existence of the hydrogen bonds in dimer, the polarized IR spectra of cinnamic acid has been studied by H.T. Flakus and M. Jabiojska [10].

Tiane-Jye Hsieh et al [11] had studied the molecular structure of cinnamic acid using the B3LYP/6-31G(d). The effect of alkali metals (Li,Na,K,Rb and Cs) on the electronic structure of cinnamic acid has been studied by means of FT-IR, FT-Raman, Nuclear Magnetic Resonance (NMR) and quantum 10 mechanical calculations [12].

The enhancement of the second harmonic generation efficiency of Sodium hydrogen phthalate single crystals when dopped with zinc has been studied by Neeti Goel et al [13].

S. Sudhahar et al have studied the effect of Sm+ rare earth ion on the structural, thermal, mechanical and optical properties of Potassium Hydrogen Phthalate single crystals. The intramolecular charge transfer, vibrational spectroscopic and the Zscan studies of nonlinear optical material Sodium acid phthalate hemihydrate has been studied by D. Sajan et al [14].

The interaction between lone pair oxygen and the σ^* orbital of O-H confirms the existence of intermolecular O-H…O hydrogen bonding which is revealed by the Natural Bond Orbital (NBO) analysis. The higher degree of conjugation between the substituent groups has also been identified.. Due to this fact they have been the objective of several experimental and theoretical studies. Synthesis, growth, optical (UV–vis–NIR absorption) and thermal (TGA/DTA) characterization of 3-Br-4'-methoxychalcone have been carried out by P.S. Patil et al [16].

V. Shettigar et al [17] have reported the 11 growth and characterization of an efficient π-conjugated potential push–pull NLO chromophore, 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one. Jose P. Abraham et al [18] have carried out an investigation on the intramolecular charge transfer of this molecule by using IR and Raman spectroscopy and Density Functional Theory (DFT) computations. The electronic effects such as induction and backdonation on the methyl hydrogen atoms have been identified from the vibrational analysis. FT-IR, FT-Raman and UV-visible spectral and the thermal analysis of 1-(4- Aminophenyl)-3-(3,4-dimethoxyphenyl)-prop-2-en-1-one have been carried out by Lynnette Joseph et al [19].

S.R. Thilagavathi et al [20] have grown Glycinium Picrate Mono Glycine crystal and measured its Second Harmonic Generation (SHG) efficiency. Although this crystal crystallizes in the centrosymmetric space group, it exhibit SHG efficiency. The theoretical and vibrational spectra of 8- hydroxyquinolinium picrate have been studied by A. Basŏglu et al [21].

A nonlinear optical crystal from the aminoacid family, l-Threoninium picrate has been grown by S. Natarajan et al [22] and its structural, spectroscopic and nonlinear optical studies have been carried out. The presence of N-H…..O hydrogen bonding has also been observed. Vibrational spectral studies and nonlinear optical properties of L-leucine Lleucinium picrate with the help of Density Functional Theory (DFT) has been carried out by Sameh Guidara et al [23]. The existence of intermolecular hydrogen bonding on this system has also been discussed.

LINEAR OPTICAL STUDIES

Linear optics is a sub-field of optics, consisting of linear systems, and is the opposite of nonlinear optics. Linear optics includes most applications of lenses, mirrors, waveplates, diffraction gratings, and many other common optical components and systems.

If an optical system is linear, it has the following properties (among others):

- If monochromatic light enters an unchanging linear-optical system, the output will be at the same frequency. For example, if red light enters a lens, it will still be red when it exits the lens.
- The superposition principle is valid for linear-optical systems. For example, if a mirror transforms light input A into output B, and input C into output D, then an input consisting of A and C simultaneously give an output of B and D simultaneously.
- Relatedly, if the input light is made more intense, then the output light is made more intense but otherwise unchanged.

These properties are violated in nonlinear optics, which frequently involves high-power pulsed lasers. Also, many material interactions including absorption and fluorescence are not part of linear optics.

Phase shifters and beam splitters are examples of devices commonly used in linear optics. In contrast, frequency-mixing processes, the optical Kerr effect, cross-phase modulation, and Raman amplification, are a few examples of nonlinear effects in optics.

The UV-VIS-NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electron in σ and π orbitals from the ground state to higher energy states. To find the transmission range of the as grown crystals, optical transmission spectrum was recorded in the range 200 to 1200 nm. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has a wide transparency window. The good transmission property of the crystal in the entire visible region ensures its suitability for second harmonic generation applications.

The optical transmission range, transparency cutoff and the absorbance band are the most important optical parameters for laser frequency conversion applications. A good transmittance in the entire UV region and lower cut off wavelength at 245 nm and at 320 nm for LA and LAAN is sufficient for SHG laser radiation of 1064 nm or other applications in the blue region. It is assigned to electronic excitation in the COO – group of L-alanine. Also in the case of UV visible spectrum of LPN single crystal which was recorded with a 2-mm-thick sample. The sample possesses a wide transparency from 295 to 1100 nm. There is no appreciable absorption of light in the entire visible range, as in the case for all amino acids.

Also the absence of any overtones and absorbance due to electronic transitions above 300 nm is an essential parameter for frequency doubling process using diode and solid-state lasers Optical transmission spectra measured on the as-grown DBLPZ compound. Below figure 1 shows lower cut off wavelength at 240 nm and there is no remarkable absorption in the entire region of the spectra. The crystal possesses good optical transparency for the second harmonic generation of Nd3+: YAG laser.

NON LINEAR OPTICS STUDY

Nonlinear Optics is a branch of optics that deals with the behavior of light in nonlinear media. It deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic fields altered in phase, frequency, amplitude or other physical properties [17]. The field of nonlinear optics finds a large intersection with theoretical and experimental physics, chemistry and engineering and has applications in all physical and life sciences. Nonlinear optical processes include processes such as harmonic generation, sum and difference frequency generation, intensity dependence of the complex refractive index, light-by-light scattering and stimulated light scattering.

Nonlinear optics remained unexplored until the discovery in 1961 of second-harmonic generation by Peter Franken et al. at University of Michigan, shortly after the construction of the first laser by Theodore Harold Maiman. However, some nonlinear effects were discovered before the development of the laser. The theoretical basis for many nonlinear processes were first described in Bloembergen's monograph "Nonlinear Optics". Nonlinear effects fall into two qualitatively different categories, parametric and non-parametric effects. A parametric non-linearity is an interaction in which the quantum state of the nonlinear material is not changed by the interaction with the optical field. As a consequence of this, the process is "instantaneous". Energy and momentum are conserved in the optical field, making phase matching important and polarization-dependent.

Some examples of nonlinear processes

- Optical Kerr effect, intensity-dependent refractive index
    - Self-focusing, an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the spatial variation in the intensity creating a spatial variation in the refractive index.
    - Kerr-lens modelocking (KLM), the use of self-focusing as a mechanism to mode-lock laser.
    - Self-phase modulation (SPM), an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the temporal variation in the intensity creating a temporal variation in the refractive index.
    - Optical solitons, an equilibrium solution for either an optical pulse (temporal soliton) or spatial mode (spatial soliton) that does not change during propagation due to a balance between dispersion and the Kerr effect (e.g. self-phase modulation for temporal and self-focusing for spatial solitons).
- Cross-phase modulation (XPM), where one wavelength of light can affect the phase of another wavelength of light through the optical Kerr effect.
- Four-wave mixing (FWM), can also arise from other nonlinearities.
- Modulational instability.
- Raman amplification
- Optical phase conjugation.
- Stimulated Brillouin scattering, interaction of photons with acoustic phonons
- Multi-photon absorption, simultaneous absorption of two or more photons, transferring the energy to a single electron.
- Multiple photoionisation, near-simultaneous removal of many bound electrons by one photon.
- Chaos in optical systems.

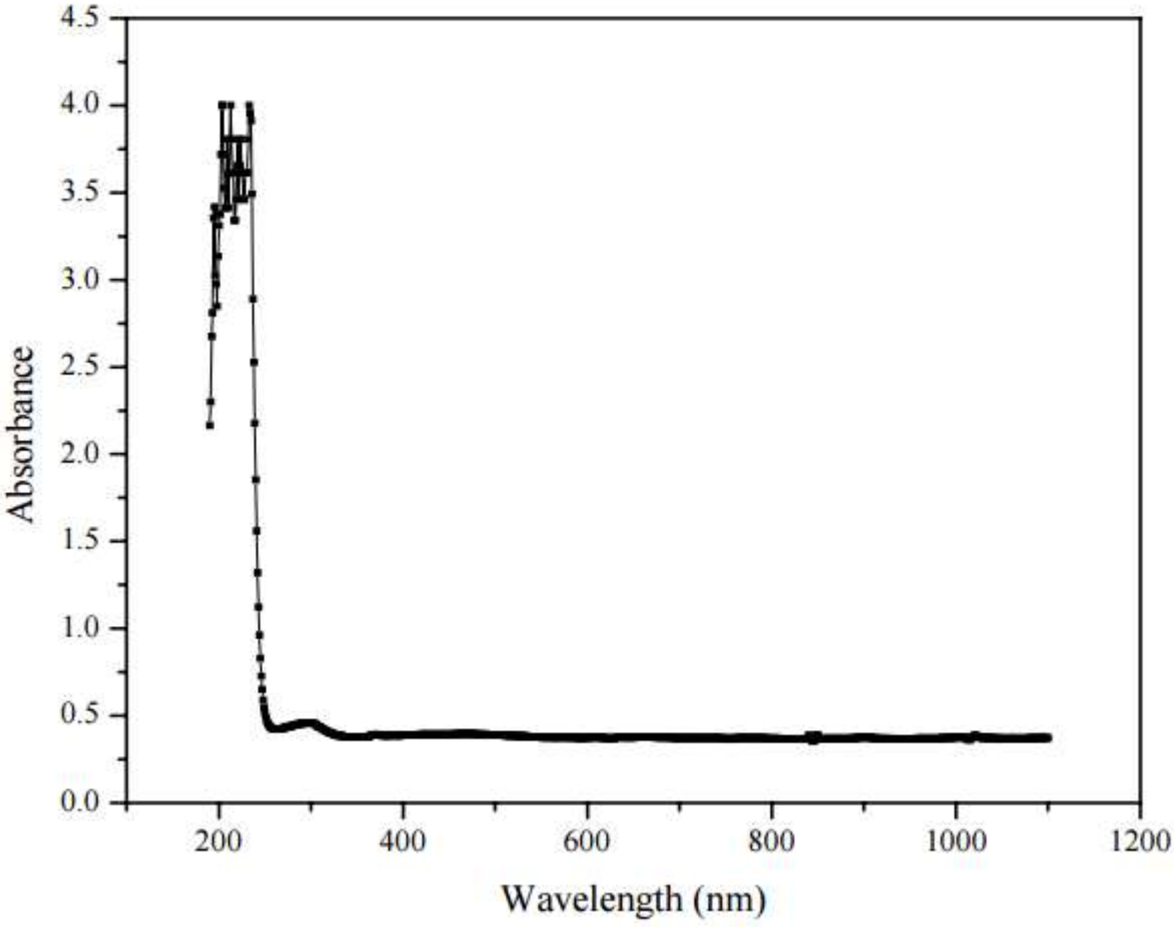

Figure 1: UV- VIS spectrum of L-alanine in linear optics

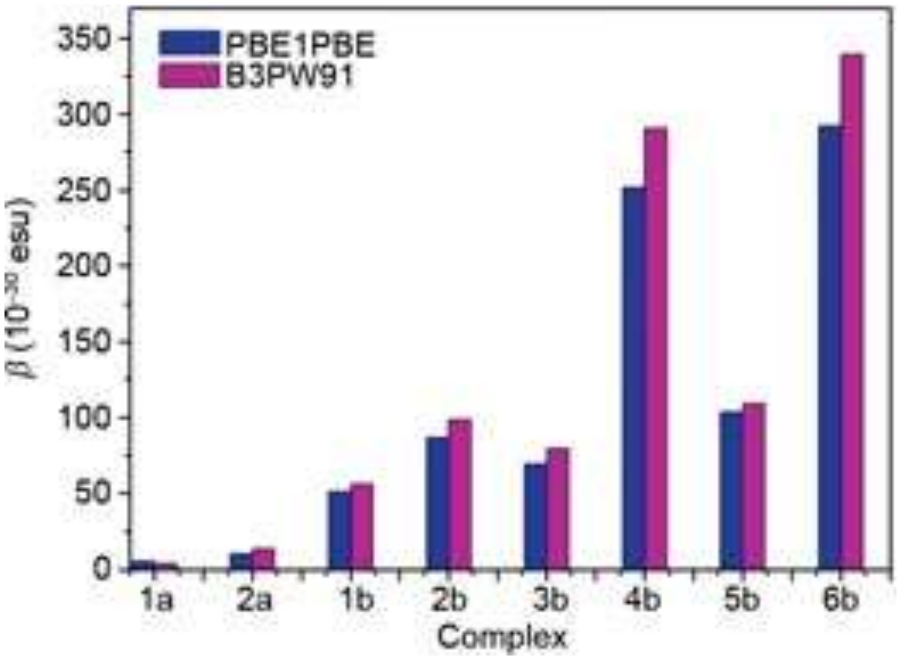

Figure 1: second-order nonlinear optical properties of some complexes

CONCEPT OF DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. Computational costs are relatively low when compared to traditional methods, such as exchange only Hartree-Fock theory and its descendants that include electron correlation.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions (of critical importance to understanding chemical reactions), especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces, dopant interactions and some other strongly correlated systems; and in calculations of the band gap and ferromagnetism in semiconductors. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules).

Although density functional theory has its conceptual roots in the Thomas–Fermi model, DFT was put on a firm theoretical footing by the two Hohenberg–Kohn theorems (H–K). The original H–K theorems held only for non-degenerate ground states in the absence of a magnetic field, although they have since been generalized to encompass these.

The first H–K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates. It lays the groundwork for reducing the many-body problem of N electrons with 3N spatial coordinates to 3 spatial coordinates, through the use of functionals of the electron density. This theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states.

The second H–K theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

APPLICATIONS OF DENSITY FUNCTIONAL THEORY (DFT)

Density Functional Theory finds application in determining various properties which can be found using various experimental setup. In general, density functional theory finds increasingly broad application in the chemical and material sciences for the interpretation and prediction of complex system behavior at an atomic scale. Specifically, DFT computational methods are applied for the study of systems to synthesis and processing parameters. In such systems, experimental studies are often encumbered by inconsistent results and non-equilibrium conditions. Examples of contemporary DFT applications include studying the effects of dopants on phase transformation behavior in oxides, magnetic behaviour in dilute magnetic semiconductor materials and the study of magnetic and electronic behavior in ferroelectrics and dilute magnetic semiconductors. Also, it has been shown that DFT has a good results in the prediction of sensitivity of some nanostructures to environment pollutants like SO2 or Acrolein as well as prediction of mechanical properties.

Phase Transformations: We can predict various phase transformations that takes place under mechanical strain. Crystal structure changes even when dimension of the system is altered for example ZnO in Wurtzitic in bulk but it is Graphitic in nanowire this can be predicted by DFT; calculating cohesive energy per atom of the system we can predict the phase transformations.

Structural properties: It can predict the best possible crystal structure with out any input of experimental data what so ever. Geometries of various organics molecules can be determined. Defect structure as vacancy, grain boundary etc can be estimated. Surface structures and adsorption can be predicted for variety of systems.

Experimentally structural properties are determined using X-ray and neutron diffraction. Various types of microscopy can also determine structural properties

Mechanical properties: We can predict various mechanical properties of given material.

Elastic Modulus:

Compressibility:

Thermal expansion coefficients:

Experimentally mechanical properties can be determined using tensile test, hardness test (Vicker and Rockwell). Thermal expansion can be determined using X-ray diffraction.

Thermodynamic properties: Formation energy of the materials can be estimated.

Transport properties: Diffusion rate of vacancy, interstitial etc. can be quantified by calculating migration barrier to diffusion of these species.

Vacancy, interstitial have to be measured with various composition to get diffusion rate.

Electronic and electrical properties: Band structure can be calculated of almost any given system. Dipole moment of molecule, interface can be calculated. Conductivity of materials can be found. Ionization energies and electron affinity can be estimated. Dharma describe the method to calculate electron affinity in his term paper.[8] Band offset can be calculated at hetero-junctions.

Band strucure can be plotted using technique as Auger effect. Conductivity can be measured Four-probe method. Ionization energy and affinity is measured using Low Energy Electron Ionization and Chemical Ionization Mass Spectrometry.

Optical properties: Though band gap is underestimated by DFT. But change in band gap (trend in band gap) with strain can be very well approximated. Hence optical spectra can be estimated. Luminescence and fluorescence of materials can be found using DFT.

Band gap, luminescence and fluorescence can be measured using UV-Visible spectroscopy.

Magnetic properties: Magnetic properties as frequency-dependent polarizabilities, frequency-dependent optical rotation parameters and magnetic susceptibilities.

Chemical properties: Rate of reaction can be determined if we know what is formation energy. Chemi-soprtion of various gases at various surface can be established.

Rate of reaction and surface adsorption properties can be determined by measuring compounds one is looking for.

CONCLUSION

In this paper, the author has studied the linear and non linear optical responses in terms of density functional theory. DFT calculations have become a popular tool in theoretical organic chemistry because of their efficiency. Energies and thermodynamic properties can be calculated. The results for enthalpies of formation are frequently not satisfactory, therefore it is advisable to consider only energy or enthalpy differences of similar structures, e.g., in reaction pathways. All kinds of spectroscopic data can be calculated, at least for the gas phase (IR, UV/VIS, NMR, EPR). Regarding NMR, the quality of calculated chemical shifts is comparable to that obtained from chemical shift prediction (based on databases and increment systems), but they are based on the full three-dimensional structure and not simply on connectivities.

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