

Original article

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CALCULATION OF THE RELATIVE PERMITTIVITY OF RHODAMINE 6G USING THE QUANTUM MECHANICAL METHOD

Iuliia Riabenko^{1,2,*} , Sergey Shulga¹ , Konstantin Beloshenko¹ 

¹ School of radiophysics, biomedical electronics and computer systems,

V. N. Karazin Kharkiv National University, 4 Svobody Sq., Kharkiv, 61022 Ukraine

² Institute of Physical Chemistry, Abbe Center of Photonics, Friedrich Schiller University Jena, Albert-Einstein-Straße 9, 07745 Germany

*Corresponding author: jriabenko@karazin.ua, iuliia.riabenko@uni-jena.de

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Background: The article describes a method for calculating the permittivity of organic molecules in quantum mechanics using the well-studied Rhodamine 6G molecule as an example. The study of optical properties of large organic molecules requires not only experimental data but also the use of calculations obtained both analytically and numerically.

Objectives: Methods for calculating permittivity as phenomenological characteristics of a sample are to be tested on well-studied molecules to be further applied to more complex nonlinear structures. However, the integral changes need to be approximated in the wave functions of large molecules.

Material and methods: The numerical simulations in MATLAB were carried out to be compared with the data from Gaussian 09, which are accurate for such small molecules as Rhodamine 6G. MATLAB calculated permittivity values for the frequency domains corresponding to absorption and fluorescence based on the Fermi golden rule. Hence, any molecule can be represented as a composite quantum mechanical system. Meanwhile, Gaussian 09 used the DFT method to determine permittivity.

Results: The Fermi golden rule can be applied due to the representation of the molecule as a complex quantum mechanical system. The proposed numerical methods minimize error by using the Dirac delta function. According to our hypothesis, the sum of the wave function of a particle in a potential well and a particle in a ring equals the wave function of the entire system, thus making it possible to study large molecules. As a result of the calculation for two wavelengths of 337 and 573 nm, the permittivity results calculated using the proposed method in MATLAB are 2.98 and 6.27, respectively. Gaussian 09 calculated the same parameters at 2.85 and 6.23.

Conclusion: The resulting datasets show a high degree of correlation. Therefore, the research hypothesis has been confirmed. The selected method also proved efficient, hence the enhancement of luminescence can be achieved by changing the relaxation time of the excited state. Plasmonic nanostructures with predetermined properties will controllably enhance the resulting field by the square of the superposition modulus of their near-field. Consequently, conditions for highly coherent radiation with high intensity and polarization can be predicted and calculated before an experiment is carried out.

KEYWORDS: DFT method; Fermi golden rule; Dirac delta function; luminescence; Rhodamine 6G; wave function.

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Dyes include polyatomic molecules with an intense absorption band in the visible and ultraviolet regions of the spectrum [1]. Benzene, pyridine or other rings constitute the structural basis of such molecules [2]. Interest in such structures is dictated by the phenomenon of luminescence [3]. Rhodamine 6G is one of the most well-studied dyes ($\lambda \approx 0.5 - 0.7 \mu m$) characterized by a high stimulated emission cross-section [4]. Although most Rhodamine dyes used to be studied in solutions [5–7], recently there has been a growing interest in the electronic properties of dyes at the interfaces between media [8–10]. Recent studies present calculations of the optical response in dyes based on the ab initio molecular dynamics [11, 12] at varying emission wavelengths, line widths, intensities, and lifetime [13, 14]. The DFT method established the eigenvalue of a molecule's molecular Hamiltonian and stationary states in a molecule [15, 16]. However, this method is inapplicable to permittivity calculations as it does not comprehensively understand wave functions corresponding to the relevant stationary states. The current research aims to describe the spectra of laser radiation within a model based on quantum mechanics and to verify the suggested model.

The structure of energy levels in the molecules of dyes can be represented by singlet S and triplet T electronic states [17]. The energy levels of the Rhodamine 6G dye are shown in Fig. 2. The energy state between vibrational levels is about $0,19 eV$, while between rotational levels, it reaches around $0,01 eV$ [19]. The broadening of the electronic energy level in the solution is larger than the energy gap between the rotational levels. For this reason, spin selection criteria determine possible combinations of transitions between/within electronic states at rotational levels, while the electronic states represent virtually continuous zones of permitted energy [20].

When light is absorbed, the molecule transitions from a lower energy level S_0 to an excited level S_1 . Due to a rapid thermal relaxation ($\tau r \sim 10^{-12} s$) [3] at the energy level S_1 , electrons move to lower vibrational levels. A spontaneous transition to the level S_0 is associated with fluorescent radiation. Thus, in dye solutions, optical excitation can lead to a population inversion from the upper vibrational levels of the S_0 band to the lower ones of the S_1 band. Amplification of light is observed at the frequencies corresponding to fluorescence. The resulting data can be used in order to calculate luminescence of Rhodamine 6G. Further enhancing luminescence can be accomplished with high-quality resonant systems [21–22], widely used in nanophotonics.

MATERIAL AND METHODS

The large size of the dye molecule [23] determines the high value of the matrix element of the dipole moment μ of the molecule [24], since the electrons involved in the absorption of light are "smeared" almost over the entire volume of the molecule. Consequently, the absorption coefficient $k \sim |\mu|^2$ [25] can also reach values which determine significant absorption of light in solutions even at a low carrier concentration, which gives the solution a color that supplements the absorption spectrum. But it also implies that an increase in fluorescence is associated with permitted dipole transitions $S_1 \rightarrow S_0$.

The description of permittivity is usually [26] associated with point dipoles subject to forced oscillations under the action of an external wave field. In this case, dissipation of energy leads to oscillation damping when the external field is removed. Thus, in a system consisting of point dipoles, the incident radiation can be absorbed, scattered. It can also have no interaction with the medium (in this case, the material is transparent in a given spectral domain) [27]. If the incident wave is represented as a monochromatic plane wave propagating along the z -axis, it can be expressed with the following equation:

$$\vec{E}_{in}(\vec{r}, t) = \vec{E}_0 e^{i(kz - \omega t)}, \quad (1)$$

where $\vec{E}_{in}(\vec{r}, t)$ is the incident field; k stands for the wave vector; ω refers to incident frequency. Polarization of the medium is expressed as follows:

$$\vec{d}(\vec{r}, t) = \varepsilon_0 \chi(\omega) \vec{E}(\vec{r}, t), \quad (2)$$

where $\vec{d}(\vec{r}, t)$ is the dipole moment of the medium-related unit of volume and $\chi(\omega)$ refers to medium polarizability.

Then the field formed by point dipoles can be described as:

$$\vec{E}_M(\vec{r}, t) \sim -z \frac{\partial \vec{d}}{\partial t} = i\omega z \vec{d}(\vec{r}, t). \quad (3)$$

The resulting field in the medium can be described with the following equation:

$$\vec{E}_{total} = \vec{E}(\vec{r}, t) + \vec{E}_m(\vec{r}, t). \quad (4)$$

In classical electrodynamics, the presence of a group of dipoles causes a phase shift in a field located within a medium or at its boundary. The phase, as mentioned earlier, shift leads to both a weaker field (a change in the modulus of the E_{total} vector) and a change in the direction of wave propagation (phase of the E_{total} vector). A specific case of such a shift to be cited is a mirror that changes the phase of the reflected wave by π .

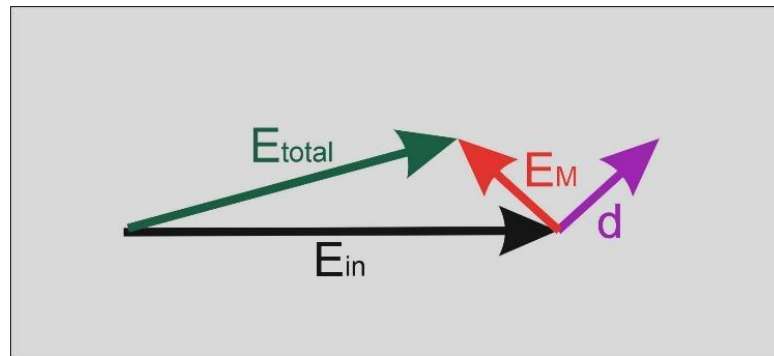


Fig. 1. Vector diagram of field superposition in the sample.

If viewed as a system in quantum mechanics, a molecule [18] can be viewed as a point dipole changing its dipole moment over time. Taking into account this difference, we cannot average the polarizability of the medium over time. Consequently, we have to consider the molecule's lifetime in the excited state and its nonradiative relaxation time. The calculations in this article were based on dried samples. Thus, the mechanism of fluorescence connected with permittivity is modeled as follows:

1. Luminescence in Rhodamine 6G is represented as a two-level system;
2. Dipole moment operators are established for each transition, while the wave functions are presented for the particle in the ring [28];
3. The level population is calculated with the help of the Fermi Golden Rule [29];
4. The equation is used to calculate the permittivity [30];
5. Calculations using MATLAB are carried out [31];
6. The results are compared to those obtained using Gaussian 09 [32].

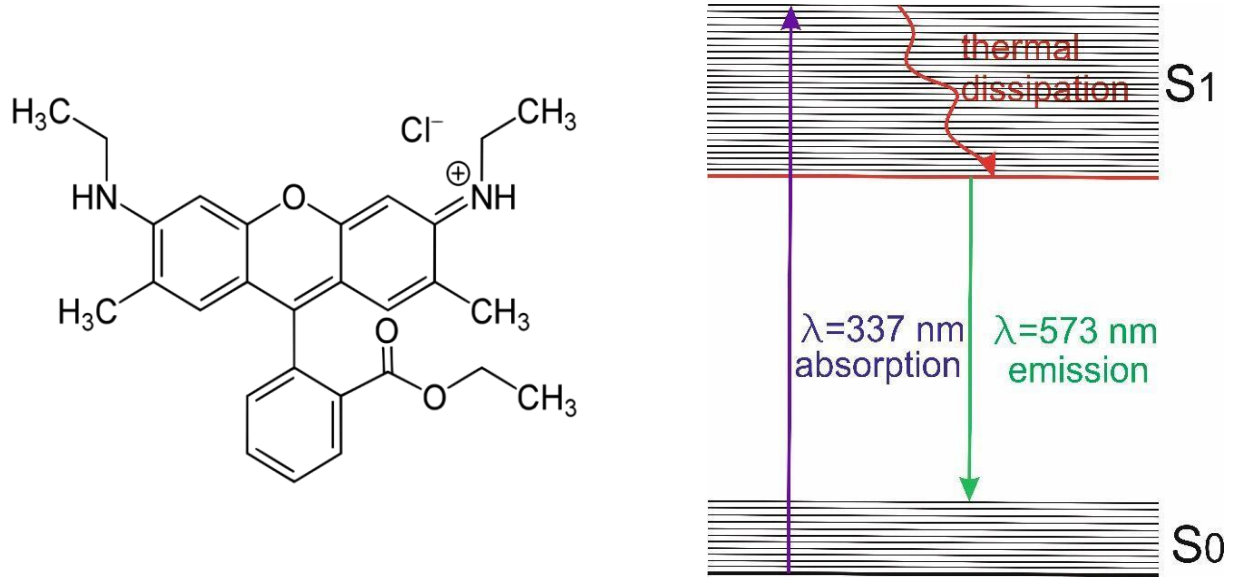


Fig. 2. Yablonsky diagram of Rhodamine 6G energy levels and its structural formula.

The permittivity of the medium, which takes into account quantum mechanical effects, can be represented as [33]:

$$\tilde{\epsilon} = 1 + \frac{32\pi^2 N \epsilon_0}{3\hbar} \sum_j \frac{|d_{ji}|^2}{\omega_{ji}^2 - \omega^2 + i\Gamma\omega} = 1 + \frac{32\pi^2 \epsilon_0}{3\hbar} \left[\frac{N_1 |d_{13}|^2}{\omega_{13}^2 - \omega^2 + i\Gamma\omega} + \frac{N_2 |d_{21}|^2}{\omega_{21}^2 - \omega^2 + i\Gamma\omega} + \frac{N_3 |d_{32}|^2}{\omega_{32}^2 - \omega^2 + i\Gamma\omega} \right], \quad (5)$$

where N is the population of the level, ϵ_0 — vacuum permittivity, \hbar — Planck's constant, d_{ji} — transition dipole moment operator and ω_{ij} — frequency of transition from level i to level j .

In the first approximation, we observe transition to excited vibrational sublevels of the S_1 level with the dipole moment d_{13} and the transition frequency ω_{13} . It is followed by nonradiative relaxation to the lower vibrational sublevels of the S_1 level with the dipole moment d_{32} and the transition frequency ω_{32} . The last radiative transition goes from the lower vibrational sublevels of the S_1 level to the upper vibrational sublevels of the S_0 level having the dipole moment d_{21} and the transition frequency ω_{12} . Meanwhile, energy levels broadening depends on the lifetimes in states i and j [34]:

$$\Gamma = \frac{1}{2} \left[\frac{1}{\tau_i} + \frac{1}{\tau_j} \right]. \quad (6)$$

The dipole moment operator is calculated based on the volume of the entire molecule [35]:

$$d_{ji} = \langle \varphi_i | = \int_V \varphi_j (ea + \vec{D}_s) \varphi_i, \quad (7)$$

where a is the radius of the excited electron orbit and D_s is the dipole moment of the structure.

The wave functions of a particle in a ring can be expressed as follows [28]:

$$\varphi_n = \frac{1}{\sqrt{2\pi}} e^{in\frac{\vec{r}}{R}}. \quad (8)$$

R -ring radius, $n = 0, \pm 1, \pm 2, \dots$ quantum numbers of state

$$\vec{d} = ea + \vec{D}_s. \quad (9)$$

The N_1, N_2, N_3 3 levels population is calculated according to the Fermi golden rule [33]:

$$W^{(1)} = \frac{2\pi}{\hbar} |V_{ij}|^2 \delta(\omega_j - \omega_i - \omega), \quad (10)$$

$$N_i = W^{(1)}\tau_i, \quad (11)$$

where $\delta(\omega_j - \omega_i - \omega)$ — Dirac delta distribution and \hat{V}_{ij} — the element which can be calculated as:

$$\hat{V}_{ij} = \frac{1}{2} \vec{E} \vec{d}. \quad (12)$$

The non-radiative transition shown as the third term in the formula (5) of permittivity, taking into account thermal radiation, is represented as follows [36]:

$$\varepsilon = \frac{2}{\varepsilon_0} \frac{cu}{|E|^2}, \quad (13)$$

where u is the electromagnetic density of thermal radiation [33]:

$$u = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}. \quad (14)$$

Where k is Boltzmann's constant, T — thermodynamic temperature, E — electric field tension can be determined as a superposition of the electric field formed by the nucleus and the rest of electrons that are not involved in the radiationless transition.

RESULT AND DISCUSSION

Permittivity was calculated in MATLAB. The input data are given in Table 1.

Table 1. Initial data [37] for the numerical calculation of the permittivity

Radius of the Rhodamine 6G ring (from Gaussian 09)	9102×10^{-9} m
Lifetime on the ground vibration S0 level	10×10^{-6} s
Lifetime on the S1 ground vibration energy level	10×10^{-8} s
Lifetime on the S1 higher vibration energy level	10×10^{-9} s
Absorption frequency	5.589×10^{15} s ⁻¹
Emission frequency	3.287×10^{15} s ⁻¹
Nonradiation transition frequency	2.302×10^{15} s ⁻¹

The data obtained due to simulation in MATLAB were verified through calculations in Gaussian 09. The interactive chemical structure model of the molecule is shown in Fig. 2 (from Avogadro 1.1.1). The calculation was carried out using a method based on the Hartree-Fock theory without imposing symmetry restrictions but with the DFT functional, which is an economical method for including electron correlations with a three-parameter density functional — Becke3LYP (B3LYP). The OPT method optimized the geometry using the basis set of cc-pVDZ orbitals. The DFT method calculated the molecular properties of the Rhodamine 6G, and then the Clausius-Mossotti approximation was used to determine the permittivity [38, 39]. The calculated values of permittivity obtained in MATLAB and calculated in Gaussian 09 are shown in Table 2.

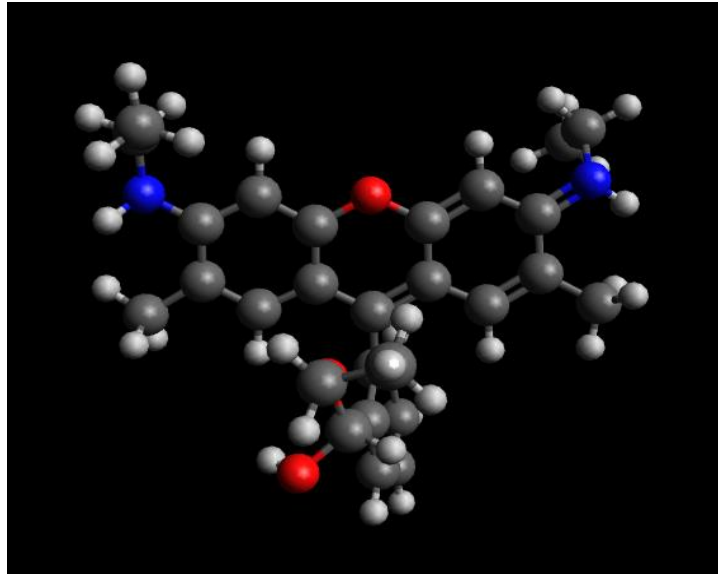


Fig. 3. The interactive chemical structure model of the Rhodamine 6G molecule.

Table 2. Calculation of permittivity for two wavelengths

	B3YP/cc-pVDZ	MATLAB
ϵ	2.85 ($\lambda=337$ nm)	2.89 ($\lambda=337$ nm)
ϵ	6.23($\lambda=573$ nm)	6.27($\lambda=573$ nm)

Permittivity generally depends on the lifetime of the molecule in an excited state as well as on the nonradiative transition time. Therefore, it is possible to change permittivity by modifying the relaxation time of the excited state. This approach is used to enhance the luminescence by amplifying the local field. In this case, the analysis of formula (10) provides a better understanding of the conditions where the maximum enhancement is reached. In this case, the phase difference between the incident wave and the electric dipole can be divided by $m\pi$. Such enhancement applies to plasmonic nanostructures. These structures transform the incident field into a surface wave [40], where the electric field vector is parallel to the medium polarizability vector. The resulting field is amplified in proportion to the square of the near-field superposition modulus, which allows controlling enhancement of the dye luminescence by creating a predetermined near field.

Currently, numerical calculations are based on RCWA and FDTD methods which involve permittivity convolution [41, 42]. A supercomputer is often required in order to perform the

calculations needed. In the case of large and complex biophysical systems, it is impossible to perform calculations in nonlinear media where the permittivity depends on the exciting electric field. Primarily, it is due to the fact that the presence of float point accuracy [43] leads to the Gibbs phenomenon [44]. On the other hand, the dynamic matrix of permittivity cannot be used in convolution [32]. Thus, a robust method is required in order to avoid the difficulties described above when performing calculations for complex nonlinear biophysical systems. The new and original method proposed can be applied for this purpose. It considers a quantum mechanical system in the electrodynamic approximation where a discrete continuum of energy interacts with a continuous one.

CONCLUSION

The paper presents a numerical method for permittivity calculation using a quantum mechanics approach. The representation of a molecule as a complex quantum mechanical system makes it possible to use the Fermi golden rule. The wave function of such a system for a small molecule of Rhodamine 6G can be presented as the sum of the wave functions for a particle in a potential well and a particle in a ring. The wave equation for large molecules is difficult to solve with Gaussian 09 as it requires much time and a supercomputer. Sometimes, it is not possible at all due to the accumulation of system errors when calculating the electronic structure of atoms. Applying the proposed numerical methods minimizes the error due to the Dirac delta function. Therefore, numerical simulation for MATLAB is relevant to establish the optical characteristics of molecules of any size. In this paper, the data obtained from MATLAB were compared with the calculations carried out in Gaussian 09. As a result of the calculation for two wavelengths of 337 and 573 nm, the permittivity results calculated using the proposed method in MATLAB are 2.98 and 6.27, respectively. Gaussian 09 calculated the same parameters at 2.85 and 6.23. The resulting data show a high degree of correspondence, which confirms that representation of the quantum mechanics properties of Rhodamine 6G is functional and the selected numerical method is valid.

These results are important for studying more complex molecules, such as toxins or nucleic acids. Integral changes in the wave functions of complex molecules can also be represented as a sum of wave functions describing changes in the structural parts of a large molecule. Nevertheless, the core of large molecules can cause disturbances that should be considered. The proposed numerical method can be further used to verify experimental data on the optical properties of molecules. This technique makes it possible to predict the optical properties of nanostructures and carry out theoretical calculations of the conditions for highly coherent radiation of high intensity and a high degree of polarization. Permittivity describes both the molecule's optical response as well as the medium's response, which can refer to any solution or solid. The working hypothesis of new research may be to test this method on wet data since this article only considered dried samples.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

Authors' ORCID ID

Iuliia Riabenko  <https://orcid.org/0000-0001-8682-8009>

Sergey Shulga  <https://orcid.org/0000-0002-9392-9366>

Konstantin Beloshenko  <https://orcid.org/0000-0002-9387-3147>

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РОЗРАХУНОК ВІДНОСНОЇ ДІЕЛЕКТРИЧНОЇ ПРОНИКНОСТІ РОДАМІНУ 6G КВАНТОВО-МЕХАНІЧНИМ МЕТОДОМ

Юлія Рябенко^{1,2*}, Сергій Шульга¹, Костянтин Білошенко¹

¹Факультет радіофізики, біомедичної електроніки та комп'ютерних систем,

Харківський національний університет імені В. Н. Каразіна, майдан Свободи, 4, м. Харків, 61022 Україна;

²Інститут фізичної хімії, Центр фотоніки Аббе, Йенський університет ім. Фрідріха Шіллера,

Альберт-Ейнштейн-Штрассе, 9, 07745 Німеччина

*e-mail: jriabenco@karazin.ua, iuliia.riabenco@uni-jena.de

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Актуальність. У статті описано квантово-механічний метод розрахунку діелектричної проникності органічних молекул на прикладі добре вивченої молекули Родаміну 6G. Вивчення оптичних властивостей великих органічних молекул вимагає не тільки експериментальних даних,

а й використання розрахунків, отриманих як аналітичним, так і чисельним шляхом.

Мета. Методи розрахунку діелектричної проникності як феноменологічної характеристики зразка повинні бути перевірені на добре вивчених молекулах, щоб надалі застосовуватися до більш складних нелінійних структур. Однак інтегральні зміни хвильових функцій великих молекул необхідно апроксимувати.

Матеріал і методи. Чисельне моделювання в MATLAB було проведено для порівняння з даними Gaussian 09, які є точними для таких не великих молекул, як Rhodamine 6G. У MATLAB було розраховано значення діелектричної проникності для частотних областей, що відповідають поглинанню та флуоресценції, на основі золотого правила Фермі. Отже, будь-яку молекулу можна представити як складну квантовомеханічну систему. У Gaussian 09 був використаний метод DFT для визначення діелектричної проникності.

Результати. Золоте правило Фермі можна застосувати завдяки представленню молекули як складної квантовомеханічної системи. Запропоновані чисельні методи мінімізують похибку за допомогою дельта-функції Дірака. Згідно з нашою гіпотезою, сума хвильових функцій частинки в потенційній ямі та частинки в кільці дорівнює хвильовій функції всієї системи, що дає можливість досліджувати великі молекули. В результаті розрахунку для двох довжин хвиль 337 та 573 нм, результати діелектричної проникності обчислені за допомогою запропонованого метода в MATLAB дорівнювали 2,98 та 6,27, відповідно. Ці самі параметри обчислені за допомогою Gaussian 09 дорівнювали 2,85 та 6,23.

Висновок. Порівняння результатів показує високий ступінь відповідності між наборами даних. Отже, гіпотеза та вибір методу були вірними. Посилення люмінесценції можна досягти зміною часу релаксації збудженого стану. Плазмонні наноструктури із задалегідь визначеними властивостями можуть керувати посилююче поле на квадрат модуля суперпозиції їх ближнього поля. Отже, умови для висококогерентного випромінювання з високою інтенсивністю та поляризацією можна передбачити та розрахувати до експериментів.

КЛЮЧОВІ СЛОВА: метод DFT; Золоте правило Фермі; дельта-функція Дірака; люмінесценція; Родамін 6G; хвильова функція