SPECTROSCOPIC FACTORS OF DIATOMIC MOLECULES: OPTIMIZED GREEN’S FUNCTIONS AND DENSITY FUNCTIONAL METHOD

It is presented an advanced approach to computing the spectroscopic factors of the diatomic molecules, which is based on the hybrid combined density functional theory (DFT) and the Green’s-functions (GF) approach. The Fermi-liquid quasiparticle version of the density functional theory is modified and used. The density of states, which describe the vibrational structure in photoelectron spectra, is defined with the use of combined DFT-GF approach and is well approximated by using only the first order coupling constants in the optimized one-quasiparticle approximation. Using the combined DFT-GF approach to computing the spectroscopic factors of diatomic molecules leads to significant simplification of the calculation procedure and increasing an accuracy of theoretical prediction.

1. Introduction

In this paper we study the problem of calculating the important spectroscopic characteristics of multielectron systems (atoms and molecules), namely, the spectroscopic factor. The spectroscopic factor is one of the most important characteristics of atomic and molecular systems and the precise information about it is very important for many applications [1-38]. The theoretical determination of spectroscopic factor for multielectron atomic and molecular systems is a rather complicated task, since in the framework of traditional a priori methods it is reduced to a calculation of corrections of perturbation theory of the type:

$$\sum_i |V_{ij}|^2/(\varepsilon_i - \varepsilon_j)$$

with summation over a large number of intermediate states. The spectroscopic factor is usually experimentally determined using inelastic scattering of fast electrons, as well as photoelectron spectroscopy (see [1]). In this case, as a rule, there is a discrepancy between the results of measurements of spectroscopic factors in these experiments caused by the influence of many electronic correlations in the initial state of the multielectron system.

In this paper we present an advanced approach to computing the spectroscopic factors of the diatomic molecules within the hybrid combined density functional theory (DFT) in the Fermi-liquid formulation and the Green’s-functions (GF) approach to quantitative determination of the spectroscopic factors for some molecular systems. The approach is based on the Green’s function method (Cederbaum-Domske version) [1,2] and Fermi-liquid DFT formalism [3-7] and using the novel effective density functionals (see also [11-22]). It is important that the calculational procedure is significantly simplified with using the quasiparticle DFT formalism.

As usually (see details in refs. [1,4,7]), the quantity which contains the information about the ionization potentials (I.P.) and molecular vibrational structure due to quick ionization is the density of occupied states:

$$N_k(\varepsilon) = (1/2\pi\hbar) \int d\varepsilon e^{i\varepsilon t} \langle \psi_0 | \hat{n}_k(t) | \psi_0 \rangle,$$

where $|\psi_0\rangle$ is the exact ground state wave function of the reference molecule and $\hat{n}_k(t)$ is an electron destruction operator, both in the Heisenberg picture.
2. Theory: Density of states in one-body and many-body solution

As usually, introducing a field operator

$$\Psi(R,\theta,x) = \sum \phi(x,R,\theta)a_i(R,\theta)$$

with the Hartree-Fock (HF) one–particle functions $\phi_j$ ($\epsilon_j(R)$ are the one-particle HF energies and $f$ denotes the set of orbitals occupied in the HF ground state; $R_0$ is the equilibrium geometry on the HF level) and dimensionless normal coordinates $Q$, one can write the standard Hamiltonian as follows [2,7]:

$$H = H_E + H_N + H_R^{(1)} + H_R^{(2)},$$

$$H_E = \sum \epsilon_j(R_0)a_i^\dagger a_i + \frac{1}{2} \sum V_{ijkl}(R_0)a_i^\dagger a_j a_k^\dagger a_l - \sum_{i,j} \sum_{k,l} [V_{ijkl}(R_0) - V_{ikjl}(R_0)] a_i^\dagger a_j a_k^\dagger a_l$$

$$H_N = \hbar \sum_{i=1}^M \omega_i (b_i^\dagger b_i + \frac{1}{2})$$

$$H_R^{(1)} = 2^{-1/2} \sum_{i=1}^M \left( \frac{\partial^\omega_i}{\partial Q_{i'}} \right)_0 (b_i + b_i') \{ a_i^\dagger a_i - n_i \} + \frac{1}{4} \sum_{i=1}^M \sum_{r,s=1}^M \left( \frac{\partial^2 \omega_i}{\partial Q_{i'} \partial Q_{j'}} \right)_0 (b_i + b_i') \{ b_r + b_r' \} \{ b_s + b_s' \} a_i^\dagger a_i a_r^\dagger a_r + \delta_{rs} a_i^\dagger a_i a_s^\dagger a_s$$

$$H_R^{(2)} = 2^{-3/2} \sum_{i=1}^M \sum_{r,s=1}^M \left( \frac{\partial^3 \omega_i}{\partial Q_{i'} \partial Q_{j'} \partial Q_{k'}} \right)_0 (b_i + b_i') \{ b_r + b_r' \} \{ b_s + b_s' \} a_i^\dagger a_i a_r^\dagger a_r + \delta_{rs} a_i^\dagger a_i a_s^\dagger a_s$$

with $n_i = 1(0)$, $i \in f (i \in g)$, $\delta_{ij} = 1(0)$, $(ijkl) \in \Sigma$.

Choosing the unperturbed $H_0$ to be $H_0 = \sum \epsilon_j(R_0)a_i^\dagger a_i + H_N$, one could define GF as

$$G_{k}(\epsilon) = \pm \delta_{\epsilon k} \exp \left[ -\hbar^{-1} (\epsilon - \delta \epsilon) t \right] \cdot \sum_{\alpha} \left| \hat{N}_k \left[ U_{\alpha} \right] \right|^2 \exp (\pm \hbar \cdot \alpha N_k t),$$

where $\delta_{\epsilon k}$ is the Kronecker delta.

The interpretation of the above Hamiltonian and an exact solution of the one-body HF problem is given in refs. [1-7]. The usual way is to define the HF-single-particle component $H_0$ of the Hamiltonian (4) as in Refs. [1,4]. Correspondingly in the one-particle picture the density of occupied states is given by

$$N_0^0(\epsilon) = \frac{1}{2\pi \hbar} \int_{-\epsilon}^{\epsilon} dt \ exp \left[ -\hbar^{-1} (\epsilon - \epsilon') \right] \langle 0 \left| \hat{N}_k \left[ U_{\alpha} \right] \right| \epsilon \rangle,$$

where $\langle 0 \left| \hat{N}_k \left[ U_{\alpha} \right] \right| \epsilon \rangle$ denotes the $k$-th eigenvalue of the reference molecule and then of $N_k(\epsilon)$.
of the diagonal matrix of the one-particle energies added to matrix of the self-energy part, are the negative V. I. P. 's for a given geometry. One can write [2,4]:

\[
(VI.P)_k = -\left(\epsilon_k + F_k\right)
\]

\[
F_k = \Sigma_k \left(-\left(VI.P\right)_k\right) = \sum_{i \neq k} \frac{1}{\epsilon_i - \epsilon_k} \sum_{k} \left(\epsilon_i - \epsilon_k\right) F_k
\]

Expanding the ionic energy \(E_k^{\text{ionic}}\) about the equilibrium geometry of the reference molecule in a power series of the normal coordinates leads to a set of linear equations for the unknown normal coordinate shifts \(\delta Q_{\alpha}\) and new coupling constants:

\[
g_i = \pm \left(1 / \sqrt{2}\right) \left[\partial (\epsilon_i + F_k) / \partial Q_i\right]_0
\]

\[
y_{sp} = \pm \left(1 / \sqrt{2}\right) \left[\partial^2 (\epsilon_i + F_k) / \partial Q_i / \partial Q_i\right]_0
\]

The coupling constants \(g_i, y_{sp}\) are calculated by the well-known perturbation expansion of the self-energy part. One could write:

\[
\sum_i g_i^{(2)}(\epsilon) = \sum_{i,j,F} (\epsilon_i - \epsilon_j) Y_{ij} + \sum_{i,j,F} (\epsilon_i - \epsilon_j) Y_{ij}
\]

and the coupling constant \(g_i\) are as [17]:

\[
g_i \approx \pm \frac{1}{\sqrt{2}} \frac{\partial \epsilon_i}{\partial Q_i} \sum_k \left[-\left(VI.P\right)_k\right]
\]

The pole strength of the corresponding GF:

\[
\rho_k = \left\{1 - \frac{\partial}{\partial \epsilon} \sum_k \left[-\left(VI.P\right)_k\right]\right\}^{-1} ; \rho_k \geq 0
\]

\[
g_i = g_i^0 + q_i (\rho_i - 1)
\]

\[
g_i^0 = \pm 2^{1 / 2} \frac{\partial \epsilon_i}{\partial Q_i}
\]

3. Fermi-liquid quasiparticle density functional theory

The quasiparticle Fermi-liquid version of the DFT [3-8,31,36] is used to determine the coupling constants etc. The master equations can be obtained on the basis of variational principle, if we start from a Lagrangian of a molecule \(L_q\). It should be defined as a functional of quasiparticle densities:

\[
v_n(r) = \sum_{\alpha} w_{\alpha} |\Phi_{\alpha}(r)|^2
\]

\[
v_n(r) = \sum_{\alpha} z_{\alpha} |\nabla \Phi_{\alpha}(r)|^2
\]

\[
v_n(r) = \sum_{\alpha} n_{\alpha} [\Phi^\dagger_{\alpha} (\Phi_{\alpha} - \Phi^\dagger_{\alpha} \Phi_{\alpha})]
\]

The densities \(v_n\) and \(v_n\) are similar to the HF electron density and kinetik energy density correspondingly; the density \(v_n\) has no an analog in the HF or DFT theory and appears as result of account for the energy dependence of the mass operator \(\Sigma\). A Lagrangian \(L_q\) can be written as a sum of a free Lagrangian and Lagrangian of interaction: \(L_q = L_q^0 + L_q^{\text{int}}\), where the interaction Lagrangian is defined in the form, which is characteristic for a standard DFT (as a sum of the Coulomb and exchange-correlation terms), but, it takes into account for a mass operator energy dependence of \(\Sigma\):

\[
L_{q}^{\text{int}} = L_K - \frac{1}{2} \sum_{i,k=0} \beta_{ik} F(r_i, r_k) v_i (r_i) v_k (r_k) d\tau_i d\tau_k
\]

where \(F\) is an effective exchange-correlation interaction potential. The constants \(\beta_{ik}\) are defined in Refs. [3-5]. The constant \(\beta_{ik}\) can be calculated by analytical way, but it is very useful to keep in mind its connection with a spectroscopic factor \(F_{ei}\) [4,5]:

\[
F_{ei} = \left\{1 - \frac{\partial}{\partial \epsilon} \sum_k \left[-\left(VI.P\right)_k\right]\right\}
\]

The new element is linked with using the DFT correlation Gunnarsson-Lundqvist, Lee-Yang-Parrr functionals (c.g.[12-16]).

4. Results and conclusions

Below we present the results of calculation of the spectroscopic factors for a number of diatomic molecules, in particular, \(C_2, N_2, O_2, F_2\) in the ground state, as well as dimers of noble gases \(A^*, K^*, Kr^*, Xe^*, Kr^*\) in the lowest excited state. As the input data, the data obtained in the HF approximation [2,40] are used. For the \(C_2, N_2, O_2, F_2\) the following spectroscopic factors
were obtained for core \((F_{p}^{c})\) and valence \((F_{p}^{v})\) shells:

\[
\begin{align*}
C_2 &- F_{sp}^{c} = 0.49, \quad F_{sp}^{v} = 0.80, \\
N_2 &- F_{sp}^{c} = 0.46, \quad F_{sp}^{v} = 0.77, \\
O_2 &- F_{sp}^{c} = 0.43, \quad F_{sp}^{v} = 0.74, \\
F_2 &- F_{sp}^{c} = 0.39, \quad F_{sp}^{v} = 0.71.
\end{align*}
\]

The obtained values of spectroscopic factors make it possible to assess to a certain extent the role of various types of correlations, in particular, intra-core and intra-valent, in these molecules. Since the spectroscopic factor, by its definition, is related to the dependence of the MSS on energy not taken into account in the HF approximation (always in this approximation: \(F_{p} = 1\)), the difference \(F_{p}^{a} - F_{p}^{b}\) from 1 indicates the corresponding role of various correlation effects. In particular, for these molecules, the contribution of intra-core correlations is somewhat more significant than that of intra-valent ones, which is also confirmed in ab initio calculations (c.f., [40]). For noble gas dimers (\(a_{g}^{2}\) outer shells) \(F_{p}^{a}\) are calculated:

\[
\begin{align*}
Ar_2 &- F_{sp}^{4} = 0.58 - (R_e = 7.1 \text{a.u.},) \\
Kr_2 &- F_{sp}^{7} = 0.37 - (R_e = 7.6 \text{a.u.},) \\
Xe_2 &- F_{sp}^{10} = 0.26 - (R_e = 8.2 \text{a.u.})
\end{align*}
\]

An analysis of the data indicates presence of strong correlation effects for the molecules, a number of features in the photoionization cross section of the \(n\delta^2\) shells, namely, the possible collectivization of the \(n\delta^2g\) shells, the presence of “shadow” states in the molecules with which strong mixing takes place and to which the strength of the initial level \((1 - F_{p})\) is transmitted. Note that such effects are known in the theory of atomic photoelectric effect, namely, for noble gas atoms (Ar and others) [6,41]).

**References**

1. Köppel, H., Domcke, W., Cederbaum, L.S., Green’s function method in quantum chemistry. *Adv. Chem. Phys.* 1984, 57, 59-132

2. Cederbaum, L., Domcke, W., On vibrational structure of photoelectron spectra by the Green’s functions method. *J. Chem. Phys.* 1984, 60, 2878-2896.

3. Glushkov, A. An universal quasiparticle energy functional in a density functional theory for relativistic atom. *Opt. and Spectr.* 1989, 66(1), 31-36.

4. Glushkov, A.V. New approach to theoretical definition of ionization potentials for molecules on the basis of Green’s function method. *J. Phys. Chem.* 1992, 66, 2671-2677.

5. Glushkov, A.V. Relativistic and correlation effects in spectra of atomic systems. Astroprint: Odessa, 2006.

6. Glushkov, A.V. *Relativistic Quantum theory. Quantum mechanics of atomic systems.* Astroprint: Odessa, 2008.

7. Ignatenko, A.V., Glushkov, A.V., Lepikh, Ya.I., Kvasikova, A.S. Photoelectron spectroscopy of diatomic molecules: optimized Green’s functions and density functional approach. *Photoelectronics.* 2018, 27, 44-51.

8. Glushkov A., Khetselius O., Svinarenko A., Buyadzhi V. Spectroscopy of autoionization states of heavy atoms and multiply charged ions. TEC, 2015.

9. Ponomarenko, E.L., Kuznetsova, A.A., Dubrovskaya, Yu.V., Bakunina, E.V. Energy and spectroscopic parameters of diatomics within generalized equation of motion method. *Photoelectronics.* 2016, 25, 114-118.

10. Svinarenko, A.A., Glushkov, A. V., Khetselius, O.Yu., Ternovsky, V.B., Dubrovskaya, Yu., Kuznetsova, A., Buyadzhi, V. Theoretical spectroscopy of rare-earth elements: spectra and autoionization resonances. *Rare Earth Element*, Ed. J. Orjuela (InTech) 2017, pp 83-104

11. Glushkov, A.V., Khetselius, O.Yu., Svinarenko A.A., Buyadzhi, V.V., Ternovsky, V.B., Kuznetsova, A., Bashkarev, P. Relativistic perturbation theory formalism to computing spectra and radiation characteristics: application to heavy element. *Recent Studies in Perturbation Theory*, ed. D. Uzunov (InTech) 2017, 131-150.

12. Kobayashi, K., Kurita, N., Kumahora, H.,
Kuzatami, T. Bond-energy calculations of Cu, Ag, CuAg with the generalized gradient approximation. Phys.Rev.A. 1991, 43, 5810.

13. Lagowskij, J., Vosko, S. Analysis of local and gradient-correction correlation energy functionals using electron removal energies. J. Phys.B: At. Mol. Opt. Phys. 1988, 21(1), 203-208.

14. Guo, Y., Whitehead, M. Effect of the correlation correction on the ionization potential and electron affinity in atoms. Phys.Rev.A. 1989, 39(1), 28-34.

15. Khetselius, O.Yu., Lopatkin Yu.M., Dubrovskaya, Yu.V, Svinarenko A.A. Sensing hyperfine-structure, electroweak interaction and parity non-conservation effect in heavy atoms and nuclei: New nuclear-QED approach. Sensor Electr. And Microsyst. Techn. 2010, 7(2), 11-19.

16. Florko, T., Ambrosov, S., Svinarenko A., Tkach, T. Collisional shift of the heavy atoms hyperfine lines in an atmosphere of the inert gas. J. Phys: Conf. Ser. 2012, 397(1), 012037.

17. Khetselius, O. Relativistic perturbation theory calculation of the hyperfine structure parameters for some heavy-element isotopes. Int. J. Quant. Chem. 2009, 109, 3330–3335.

18. Khetselius, O. Relativistic calculation of the hyperfine structure parameters for heavy elements and laser detection of the heavy isotopes. Phys. Scr. 2009, 135, 014023.

19. Glushkov A.V., Atom in electromagnetic field. KNT: Kiev, 2005.

20. Khetselius, O. Yu. Hyperfine structure of atomic spectra; Astroprint: Odessa, 2008.

21. Khetselius, O.Yu. Quantum structure of electroweak interaction in heavy finite Fermi-systems. Astroprint: Odessa, 2011.

22. Khetselius, O.Y., Glushkov, A.V., Gurskaya, M.Y., Kuznetsova, A.A., Dubrovskaya, Yu.V., Serga, I.N., Vitavetskaya, L.A. Computational modelling parity nonconservation and electroweak interaction effects in heavy atomic systems within the nuclear-relativistic many-body perturbation theory. J. Phys.: Conf. Ser. 2017, 905(1), 012029.

23. Glushkov, A., Gurskaya, M., Ignatenko, A., Smirnov, A., Serga, I., Svinarenko, A., Ter-novskiy, E. Computational code in atomic and nuclear quantum optics: Advanced computing multiphoton resonance parameters for atoms in a strong laser field. J. Phys.: Conf. Ser. 2017, 905(1), 012004.

24. Ambrosov S., Ignatenko V., Korchevsky D., Kozlovskaya V. Sensing stochasticity of atomic systems in crossed electric and magnetic fields by analysis of level statistics for continuous energy spectra. Sensor Electr. and Microsys. Techn. 2005, Issue 2, 19-23.

25. Buyadzhi, V.V., Glushkov, A.V., Mansarlysky, V.F., Ignatenko, A.V., Svinarenko, A. Spectroscopy of atoms in a strong laser field: new method to sensing ac Stark effect, multiphoton resonances parameters and ionization cross-sections. Sensor Electr. and Microsys. Techn. 2015, 12(4), 27-36.

26. Svinarenko A.A., Mischenko E., Loboda A., Dubrovskaya Yu. Quantum measure of frequency and sensing the collisional shift of the ytterbium hyperfine lines in medium of helium gas. Sensor Electr. and Microsys. Techn. 2009, 1, 25-29.

27. Malinovskaya S.V., Dubrovskaya Yu.V., Zelenzova T.N. The atomic chemical environment effect on the b decay probabilities: Relativistic calculation. Herald of Kiev Nat. Univ. Ser.: Phys.-Math. 2004, N4, 427-432.

28. Glushkov A., Khetselius O., Svinarenko A., Prepelitsa G., Mischenko E., The Green’s functions and density functional approach to vibrational structure in the photoelectron spectra for molecules. AIP Conf. Proc. 2010, 1290, 263-268.

29. Khetselius O., Florko T., Svinarenko A., Tkach T. Radiative and collisional spectroscopy of hyperfine lines of the Li-like heavy ions and TI atom in an atmosphere of inert gas. Phys.Scripta. 2013, T153, 014037.

30. Glushkov, A.V., Kivganov, A.F., Khokhlov, V.N., Buyadzhi, T.V., Vitavetskaya, L.A., Borovskaya, G.A., Polishchuk, V.N. Calculation of the spectroscopic characteristics of diatomic van der Waals molecules and ions: Inert gas atom—halogen-type inert gas ion in the ground state. Russian Phys. Journ. 1998, 41(3), 223-226.

31. Glushkov, A., Malinovskii, A., Efimov, V.
Kivganov, A., Khokhlov, V., Vitavetskaya, L., Borovskaya, G., Calculation of alkaline metal dimers in terms of model perturbation theory. *J. Struct. Chem.* 1998, 39(2), 179-185.

32. Khetselius, O.Yu. Hyperfine structure of radium. *Photoelectron.* 2005, 14, 83-85.

33. Khetselius O.Yu., Quantum Geometry: New approach to quantization of the quasistationary states of Dirac equation for super heavy ion and calculating hyper fine structure parameters. *Proc. Int. Geometry Center.* 2012, 5(3-4), 39-45.

34. Dubrovskaya, Yu., Khetselius, O.Yu., Vitavetskaya, L., Ternovsky, V., Serga, I. Quantum chemistry and spectroscopy of pionic atomic systems with accounting for relativistic, radiative, and strong interaction effects. *Adv. in Quantum Chem.* 2019, Vol.78, pp 193-222.

35. Khetselius, O.Yu., Glushkov, A.V., Dubrovskaya, Yu.V., Chernyakova, Yu.G., Ignatenko, A.V., Serga, I.N., Vitavetskaya, L. Relativistic quantum chemistry and spectroscopy of exotic atomic systems with accounting for strong interaction effects. In: Wang YA, Thachuk M, Krems R, Maruani J (eds) *Quantum Systems in Physics, Chemistry, and Biology.* Springer, Cham. 2017, 30, 169

36. Glushkov, A., Ivanov, L. DC strong-field Stark effect: consistent quantum-mechanical approach. *J. Phys.B: At. Mol. Opt. Phys.* 1993, 26(14), L379 –386.

37. Glushkov, A.V., Khetselius, O.Yu., Svinarenko, A.A., Buyadzhi, V. Methods of computational mathematics and mathematical physics. P.1. TES: Odessa, 2015.

38. Glushkov, A.V., Safranov, T.A., Khetselius, O.Yu., Ignatenko, A.V., Buyadzhi, V.V., Svinarenko, A.A. Analysis and forecast of the environmental radioactivity dynamics based on methods of chaos theory: General conceptions. *Environm. Problems.* 2016, 1(2), 115-120.

39. Glushkov, A., Buyadzhi, V., Kvasikova, A., Ignatenko, A., Kuznetsova, A., Prepelitsa, G., Ternovsky, V. Non-Linear chaotic dynamics of quantum systems: Molecules in an electromagnetic field and laser systems. In: Tadjer A, Pavlov R, Maruani J etal, (eds) *Quantum Systems in Physics, Chemistry, and Biology.* Springer, Cham. 2017, 30, 169

40. Robert, C., Morrison, R., Liu, G., Extended Koopmans theorem: approximate ionization energies from MCSCF Wave Functions. *J. Comp. Chem.* 1992, 13, 1004-1010.

41. Svinarenko, A. Spectroscopy of autoionization resonances in spectra of barium. *Photoelectronics.* 2014, 23, 86-90.
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Key words: diatomic molecules, Green’s functions, density functional

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СПЕКТРОСКОПИЧЕСКИЕ ФАКТОРЫ ДЛЯ ДВУХАТОМНЫХ МОЛЕКУЛ: ОПТИМИЗИРОВАННЫЙ МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ

Резюме. Представлен усовершенствованный подход к вычислению спектроскопических факторов двухатомных молекул, базирующийся на гибридной комбинированной теории функционала плотности (ТФП) и методе функции Грина (ФГ). Используется модель ферми-жидкостная квазичастичная версия ТФП. Плотность состояний, которая описывает колебательную структуру в фотоэлектронных спектрах, определяется с использованием комбинированного подхода ТФП - ФГ. Использование комбинированного ТФП-ФГ подхода приводит к значительному упрощению процедуры расчета и повышению точности теоретического прогнозирования.

Ключевые слова: двухатомные молекулы, функция Грина, функционал плотности

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СПЕКТРОСКОПІЧНІ ФАКТОРИ ДВОАТОМНИХ МОЛЕКУЛ: ОПТИМІЗОВАНИЙ МЕТОД ФУНКЦІЙ ГРІНА І ФУНКЦІОНАЛУ ГУСТИНИ

Резюме. Представленний вдосконаленний метод обчислення спектроскопічних факторів 2-атомних молекул, що базується на гібридній теорії функціонала щільності (ТФП) і методі функції Гріна (ФГ). Використано фермі-рідинну квазічастинкову версію ТФП. Густина станів, які описує коливаальну структуру фотоелектронного спектру, визначається в межах ТФП-ФГ методу. Використання комбінованого ТФП-ФГ методу призводить до спрощення процедури обчислення, підвищення точності прогнозу.

Ключові слова: двоатомні молекули, функція Гріна, функціонал густини