

# ОПТИЧНІ, ОПТОЕЛЕКТРОННІ І РАДІАЦІЙНІ СЕНСОРИ

---

## OPTICAL AND OPTOELECTRONIC AND RADIATION SENSORS

---

---

PACS 33.20.-t; UDC 539.186

DOI <http://dx.doi.org/10.18524/1815-7459.2018.4.150505>

### PHOTOELECTRON SPECTROSCOPY OF DIATOMIC MOLECULES: HYBRID DENSITY FUNCTIONAL AND GREEN'S FUNCTIONS APPROACH TO SENSING MOLECULAR CONSTANTS

*A. V. Ignatenko, A. V. Glushkov, O. Yu. Khetselius, Yu. Ya. Bunyakova, A. A. Svinarenko*

Odessa State Environmental University, 15, Lvovskaya str., Odessa, 65016, Ukraine  
E-mail: [ignatenkoav13@gmail.com](mailto:ignatenkoav13@gmail.com)

### PHOTOELECTRON SPECTROSCOPY OF DIATOMIC MOLECULES: HYBRID DENSITY FUNCTIONAL AND GREEN'S FUNCTIONS APPROACH TO SENSING MOLECULAR CONSTANTS

*A. V. Ignatenko, A. V. Glushkov, O. Yu. Khetselius, Yu. Ya. Bunyakova, A. A. Svinarenko*

**Abstract.** It is developed the optimized version of the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach to quantitative treating the diatomic photoelectron spectra and molecular constants. The Fermi-liquid quasiparticle version of the density functional theory is 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 leads to significant simplification of the calculation and increasing an accuracy of theoretical prediction that is confirmed by computing the molecular spectral parameters for the molecules of CH, CO, HF etc.

**Keywords:** photoelectron spectra of molecules, new hybrid approach, Green's functions, density functional theory

## ФОТОЕЛЕКТРОННА СПЕКТРОСКОПІЯ ДВОАТОМНИХ МОЛЕКУЛ: ГІБРИДНИЙ МЕТОД ФУНКЦІОНАЛУ ГУСТИНИ ТА ФУНКЦІЙ ГРИНА У ВИЗНАЧЕННІ МОЛЕКУЛЯРНИХ КОНСТАНТ

*Г. В. Ігнатенко, О. В. Глушков, О. Ю. Хецеліус, Ю. Я. Бунякова, А. А. Свиначенко*

**Анотація.** Розвинута оптимізована версія гібридної комбінованої теорії функціоналу густини (DFT) і методу функцій Грина (ГФ) для кількісного опису фотоелектронних спектрів двохатомних молекул та молекулярних констант. Новий гібридний підхід суттєво базується на фермі-рідинній квазічастинній версії теорії функціоналу густини. Густина стану, яка описує коливальну структуру в фотоелектронних спектрах, визначається з використанням комбінованого DFT-GF підходу та фізично розумно апроксимується за допомогою тільки першого порядку констант зв'язку в оптимізованому одноквазічастинковому наближенні. Використання комбінованого DFT-GF підходу призводить до значного спрощення молекулярних обчислень та збільшення точності теоретичного прогнозування, що повністю підтверджується відповідними обчисленнями спектральних параметрів для молекул CH, CO, HF тощо.

**Ключові слова:** фотоелектронний спектр молекул, новий гібридний підхід, метод функцій Грина, теорія функціонала густини

## ФОТОЭЛЕКТРОННАЯ СПЕКТРОСКОПИЯ ДВУХАТОМНЫХ МОЛЕКУЛ: ГИБРИДНЫЙ МЕТОД ФУНКЦИОНАЛА ПЛОТНОСТИ И ФУНКЦИЙ ГРИНА В ОПРЕДЕЛЕНИИ МОЛЕКУЛЯРНЫХ КОНСТАНТ

*А. В. Игнатенко, А. В. Глушков, О. Ю. Хецеліус, Ю. Я. Бунякова, А. А. Свиначенко*

**Аннотация.** Разработана оптимизированная версия гибридной комбинированной теории функционала плотности (DFT) и метода функций Грина (GF) для количественного описания фотоэлектронных спектров двухатомных молекул и молекулярных констант. Новый подход существенно базируется на ферми-жидкостной квазічастичной версии теории функционала плотности. Плотность состояний, которая описывают колебательную структуру в фотоэлектронных спектрах, определяется с использованием комбинированного DFT-GF подхода и физически разумно аппроксимируется с использованием только первого порядка констант связи в оптимизированном одноквазічастичном приближении. Использование комбинированного DFT-GF подхода приводит к значительному упрощению молекулярных расчетов и увеличению точности теоретического предсказания, что полностью подтверждается расчетами молекулярных спектральных параметров для молекул CH, CO, HF и др.

**Ключевые слова:** фотоэлектронный спектр молекул, новый гибридный подход, метод функций Грина, теория функционала плотности

## 1. Introduction

The Green's function (GF) method is very well known in a quantum theory of field, quantum electrodynamics, quantum theory of solids. This approach naturally provided the known progress in treating atoms, solids and molecules, as it has been shown in many papers (c.f.[1-4]). The experimental photoelectron spectra (PES) of molecules usually show a pronounced vibrational structure [1,2]. Many papers have been devoted to treatment of the vibrational spectra by construction of potential curves for the reference molecule (the molecule which is to be ionized) and the molecular ion. Usually the electronic GF is defined for fixed position of the nuclei. The cited method, however, requires as input data the geometries, frequencies, and potential functions of the initial and final states. Since in most cases at least a part of these data are unavailable, the calculations have been carried out with the objective of determining the missing data by comparison with experiment. To avoid this difficulty and to gain additional information about the ionization process, Cederbaum et al [2] extended the GF approach to include the vibrational effects and showed that the GF method allowed *ab initio* calculation of the intensity distribution of the vibrational lines etc. For large molecules far more approximate but more easily applied methods such as DFT [3] or from the wave-function world the simplest correlated model MBPT are preferred [10]. Indeed, in the last decades DFT theory became by a great, quickly developing field of the modern computational chemistry of molecules. In Refs. [4,5] the authors underlined the elements of the generalized approach to vibrational structure in the PES of molecules, which is based on the DFT and the GF approach and presented some numerical illustrations of quantitative treating the carbon oxide molecule parameters. It is important that calculational procedure can be significantly simplified with using DFT formalism in comparison with the classical GF method realization.

In this paper we present the optimized version of the hybrid combined DFT-GF approach to quantitative treating the diatomic photoelec-

tron spectra. The approach is based on the GF method in the Cederbaum-Domske version [2], Fermi-liquid DFT formalism [6-13] and use of the novel effective density functionals (see also [14-26]). The density of states is well approximated by using only the first order coupling constants in the one-particle approximation. It is important that the calculational procedure is significantly simplified with using the quasiparticle DFT formalism. Thus quite simple method becomes a powerful tool in interpreting the vibrational structure of photoelectron spectra for different molecular systems.

## 2. The hybrid quasiparticle DFT- optimized GF approach

As usually, introducing a field operator  $\Psi(R, \theta, x) = \sum_i \phi_i(x, R, \theta) a_i(R, \theta)$  with the Hartree-Fock (HF) one-particle functions  $\phi_i(\epsilon_i(R))$  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  $Q_s$  one can write the standard Hamiltonian as follows:

$$\begin{aligned}
 H &= H_E + H_N + H_{EN}^{(1)} + H_{EN}^{(2)}, \\
 H_E &= \sum_i \epsilon_i(R_0) a_i^\dagger a_i + \frac{1}{2} \sum_{ijkl} V_{ijkl}(R_0) a_i^\dagger a_j^\dagger a_k a_l - \\
 &\quad - \sum_{i,j} \sum_{k \neq l} [V_{ijk}(R_0) - V_{ikj}(R_0)] a_i^\dagger a_j \\
 H_N &= \hbar \sum_{s=1}^M \omega_s (b_s^\dagger b_s + \frac{1}{2}), \quad H_{EN}^{(1)} = 2^{-1/2} \sum_{s=1}^M \left( \frac{\partial \epsilon_i}{\partial Q_s} \right)_0 (b_s + b_s^\dagger) [a_i^\dagger a_i - n_i] + \\
 &\quad + \frac{1}{4} \sum_{s,s'=1}^M \left( \frac{\partial^2 \epsilon_i}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b_s^\dagger)(b_{s'} + b_{s'}^\dagger) [a_i^\dagger a_i - n_i], \\
 H_{EN}^{(2)} &= 2^{-3/2} \sum_{s=1}^M \left( \frac{\partial V_{ijkl}}{\partial Q_s} \right)_0 (b_s + b_s^\dagger) [\delta v_1 a_i^\dagger a_j a_k + \\
 &\quad + \delta v_2 a_i a_k a_j^\dagger a_l + 2\delta v_3 a_j^\dagger a_k a_l a_i^\dagger] + \\
 &\quad + \frac{1}{8} \sum_{s,s'=1}^M \left( \frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b_s^\dagger)(b_{s'} + b_{s'}^\dagger) \cdot \\
 &\quad [\delta v_1 a_i^\dagger a_j a_k + \delta v_2 a_i a_k a_j^\dagger a_l + 2\delta v_3 a_j^\dagger a_k a_l a_i^\dagger]
 \end{aligned} \tag{1}$$

with  $n_i=1$  (0),  $i \in f$  ( $i \notin f$ ),  $\delta \sigma_j=1$  (0),  $(ijkl) \in \sigma_{f,\pm}$  where the index set  $v_1$  means that at least  $\phi_k$  and  $\phi_l$  or  $\phi_i$  and  $\phi_j$  are unoccupied,  $v_2$  that at most one of the orbitals is unoccupied, and  $v_3$  that  $\phi_k$  and  $\phi_j$  or  $\phi_l$  and  $\phi_i$  are unoccupied. The  $\omega_s$  are the HF frequencies;  $b_s, b_s^\dagger$  are destruction and creation operators for vibrational quanta as

$$\begin{aligned}
 Q_s &= (1/\sqrt{2})(b_s + b_s^\dagger), \\
 \partial/\partial Q_s &= (1/\sqrt{2})(b_s - b_s^\dagger).
 \end{aligned} \tag{2}$$

The interpretation of the above Hamiltonian and an exact solution of the one-body HF problem is given in refs. [1,2,4]. The usual way is to define the HF-single-particle component  $H_0$  of the Hamiltonian (4) is as in Refs. [1,5]. Correspondingly in the one-particle picture the density of occupied states is given by

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(\epsilon - \epsilon_k)t} \langle 0 | e^{\pm i\hbar^{-1}\tilde{H}_0 t} | 0 \rangle, \quad (3)$$

$$\tilde{H}_0 = \sum_{s=1}^M \hbar\omega_s b_s^\dagger b_s + \sum_{s=1}^M g_s^k (b_s + b_s^\dagger) + \quad (4)$$

$$+ \sum_{s,s'=1}^M \gamma_{ss'}^k (b_s + b_s^\dagger)(b_{s'} + b_{s'}^\dagger)$$

$$g_s^i = \pm \frac{1}{\sqrt{2}} \left( \frac{\partial \epsilon_i}{\partial Q_s} \right)_0, \quad \gamma_{ss'}^i = \pm \frac{1}{4} \left( \frac{\partial^2 \epsilon_i}{\partial Q_s \partial Q_{s'}} \right)_0. \quad (5)$$

In a diagrammatic method to get function  $N_k(\epsilon)$  one should calculate the GF  $G_{kk'}(\epsilon)$  first [1,2,5]:

$$G_{kk'}(\epsilon) = -i\hbar^{-1} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}\epsilon t} \langle \psi_0 | T \{ a_k(t) a_k^\dagger(0) \} | \psi_0 \rangle \quad (6)$$

and the function  $N_k(\epsilon)$  can be found from the relation

$$\pi N_k(\epsilon) = a \operatorname{Im} G_{kk}(\epsilon - ai\eta), \quad a = -\operatorname{sign} \epsilon_k. \quad (7)$$

Choosing the unperturbed Hamiltonian  $H_0$  to be  $H_0 = \sum (\epsilon)_i a_i^\dagger a_i + H_N$  one could define the GF as follows:

$$G_{kk'}^{OB}(t) = \pm \delta_{kk'} i \exp[-in^{-1}(\epsilon_k \mp \Delta \epsilon)t] \cdot \sum_n \langle \hat{n}_k | U_k | 0 \rangle^2 \exp(\pm in_k \cdot \hat{\omega}_k t), \quad (8)$$

The direct method for calculation of  $N_k(\epsilon)$  as the imaginary part of the GF includes a definition of the vertical I.P. (V.I.P.s) of the reference molecule and then of  $N_k(\epsilon)$ . The zeros of the functions

$$D_k(\epsilon) = \epsilon - [\epsilon^{op} + \Sigma(\epsilon)]_k, \quad (9)$$

where  $(\epsilon^{op} + \Sigma)_k$  denotes the  $k$ -th eigenvalue 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 [1]:

$$(V.I.P.)_k = -(\epsilon_k + F_k),$$

$$F_k = \Sigma_{kk}(- (V.I.P.)_k) \approx \frac{1}{1 - \partial \Sigma_{kk}(\epsilon_k) / \partial \epsilon} \Sigma_{kk}(\epsilon_k) \quad (10)$$

Expanding the ionic energy  $E_k^{N-1}$  about the equilibrium geometry of the reference molecule in a power series of the normal coordinates of this molecule leads to a set of linear equations in the unknown normal coordinate shifts  $\delta Q_s$  and new coupling constants are then:

$$g_l = \pm (1/\sqrt{2}) [\partial(\epsilon_k + F_k) / \partial Q_l]_0 \quad (11)$$

$$y_{ll'} = \pm \left( \frac{1}{4} \right) [\partial^2(\epsilon_k + F_k) / \partial Q_l \partial Q_{l'}]_0$$

The coupling constants  $g_l$  and  $y_{ll'}$  are calculated by the well-known perturbation expansion of the self-energy part. In second order one obtains:

$$\Sigma_{kk}^{(2)}(\epsilon) = \sum_{\substack{i,j \\ s \neq F}} \frac{(V_{ksij} - V_{ksji}) \mathcal{Y}_{ksij}}{\epsilon + \epsilon_s - \epsilon_i - \epsilon_j} + \sum_{\substack{i,j \\ s \neq F}} \frac{(V_{ksij} - V_{ksji}) \mathcal{Y}_{ksij}}{\epsilon + \epsilon_s - \epsilon_i - \epsilon_j} \quad (12)$$

and the coupling constant  $g_p$  are written as [2,5]:

$$g_l \approx \pm \frac{1}{\sqrt{2}} \frac{\partial \epsilon_k}{\partial Q_l} \frac{1 + q_k (\partial / \partial \epsilon) \Sigma_{kk} [-(V.I.P.)_k]}{1 - (\partial / \partial \epsilon) \Sigma_{kk} [-(V.I.P.)_k]} \quad (13)$$

The pole strength of the corresponding GF:

$$\rho_k = \left\{ 1 - \frac{\partial}{\partial \epsilon} \Sigma_{kk} [-(V.I.P.)_k] \right\}^{-1}; \quad \rho_k \geq 0, \quad (14)$$

$$g_l \approx g_l^0 [\rho_k + q_k (\rho_k - 1)]_p$$

$$g_l^0 = \pm 2^{-1/2} \partial \epsilon_k / \partial Q_l$$

The above presented results can be usefully treated in the terms of the correlation and reorganization effects. Usually it is introduced the following expression for an I.P.:

$$(I.P.)_k = -\epsilon_k - \sum_{j \in F} \frac{(V_{kij} - V_{kji})}{\epsilon_j - \epsilon_i} - \frac{1}{2} \sum_{i \in F} \frac{(V_{kijl} - V_{klij})}{\epsilon_k + \epsilon_i - \epsilon_j - \epsilon_l} (1 - \delta_{ik}) -$$

$$- \frac{1}{2} \sum_{\substack{p,q \in F \\ j \neq F}} \frac{(V_{kjpq} - V_{kjqp})^2}{\epsilon_k + \epsilon_i - \epsilon_p - \epsilon_q} (1 - \delta_{kp}) (1 - \delta_{kq}) \quad (15)$$

The first correction term is due to reorganization, the remaining correction terms are due to correlation effects. Then the coupling constant  $g_p$  can be written as

$$g_i \approx g_i^0 \left\{ 1 + \sum_{j \in F} \frac{(V_{kkkj})^2}{(\epsilon_j - \epsilon_k)^2} - \frac{1}{2} \left[ \sum_{\substack{i \in F \\ j, l \in F}} \frac{(V_{kijl} - V_{lkij})^2}{(\epsilon_k + \epsilon_i - \epsilon_j - \epsilon_l)^2} (1 - \delta_{ki}) + \sum_{\substack{p, q \in F \\ j, l \in F}} \frac{(V_{kijp} - V_{kjqp})^2}{(\epsilon_k + \epsilon_i - \epsilon_p - \epsilon_q)^2} (1 - \delta_{ki})(1 - \delta_{kp}) \right] \right\}. \quad (16)$$

The second coupling constant can be written

$$\gamma_{ii} = \gamma_{ii}^0 \left( \frac{g_i}{g_i^0} \right) + \frac{1}{4} \sqrt{2} g_i^0 \frac{\partial}{\partial Q_i} \left( \frac{g_i}{g_i^0} \right) \quad (17)$$

$\gamma_{ii}^0$ , is defined analogously  $g_i^0$ .

The key elements of novelty of our advanced theory are connected with implementation of elements of the quasiparticle Fermi-liquid version of the DFT (QFLDFT) [1-3,8,17] to the GF approach. Let us note that the QFLDFT was developed in Refs. [1-3,8,17] is used to determine the coupling constants etc. The master equations can be obtained on the basis of variational principle with using the corresponding Lagrangian of a molecule  $L_q$ . It should be defined as a functional of quasiparticle densities:

$$\begin{aligned} v_0(r) &= \sum_{\lambda} n_{\lambda} |\Phi_{\lambda}(r)|^2, \\ v_1(r) &= \sum_{\lambda} n_{\lambda} |\nabla \Phi_{\lambda}(r)|^2, \\ v_2(r) &= \sum_{\lambda} n_{\lambda} [\Phi_{\lambda}^* \Phi_{\lambda} - \Phi_{\lambda}^* \Phi_{\lambda}]. \end{aligned} \quad (18)$$

The densities  $v_0$  and  $v_1$  are similar to the HF electron density and kinetical energy density correspondingly; the density  $v_2$  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:  $L_q = L_q^0 + L_q^{int}$ , 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), however, it takes into account for the energy dependence of a mass operator  $\Sigma$ :

$$L_q^{int} = L_K - \frac{1}{2} \sum_{i,k=0}^2 \int \beta_{ik} F(r_1, r_2) v_i(r_1) v_k(r_2) dr_1 dr_2 \quad (19)$$

where  $F$  is an effective potential of the exchange-correlation interaction. The constants  $\beta_{ik}$  are defined in Ref. [7]. The single used constant  $\beta_{02}$  can be calculated by analytical way, but it is very useful to remember its connection with a spectroscopic factor  $F_{sp}$  of the system [7]:

$$F_{sp} = \left\{ 1 - \frac{\partial}{\partial \epsilon} \sum_{kk} [-(V.I.P.)_k] \right\} \quad (20)$$

The terms  $\partial \Sigma / \partial \epsilon$  and  $\Sigma_2$  is directly linked [6]. In the terms of the Green function method expression (7) is in fact corresponding to the GF pole strength. The new element of an approach is connected with using the DFT correlation functionals, in particular, the Gunnarsson-Lundqvist, Lee-Yang-Parr ones etc. (look details in ref. [1,22]).

### 3. Some results and conclusions

In further calculation as potential  $V_{XC}$  we use the exchange-correlation pseudo-potential which contains the correlation (Gunnarsson-Lundqvist) potential and relativistic exchanger Kohn-Sham one [1,3]. As an object of studying we choose the diatomic molecules of HF, CH, CO for application of the combined Green's function method and quasiparticle DFT approach. In refs. [2,4] it was presented an analysis and calculation of the photoelectron spectrum for the sufficiently complicated from the theoretical viewpoint molecules such as the  $N_2$  and CO molecules, where the known Koopmans' theorem even fails in reproducing the sequence of the V. I. P.'s in the PES spectrum [1-3]. It is stressing, however it has been possible to get the full sufficiently correct description of the diatomics PES already in the effective one-quasiparticle approximation [1,2,5]. Another essential aspect is sufficiently simple calculational procedure, provided by using the DFT. Moreover, here the cumbersome calculation is not necessary, if the detailed Hartree-Fock (Hartree-Fock-Roothaan) data (separate HF-potential curves of molecule and ion) for the studied diatomic molecule are available. Further it is easily



to estimate the pole strengths  $p_k$  and the values  $q_k$ . When the change of frequency due to ionization is small, the density of states can be well approximated using only one parameter  $g$ :

$$N_k(\epsilon) = \sum_{n=0}^{\infty} e^{-S} \frac{S^n}{n!} \delta(\epsilon - \epsilon_k + \Delta \epsilon_k + n \cdot \hbar \hat{\omega}),$$

$$S = g^2 (\hbar \omega)^{-2} . \quad (21)$$

In case the frequencies change considerably, the intensity distribution of the most intensive lines can analogously be well approximated by an effective parameter  $S$ . Below we mean that  $S^0$  denotes the constant  $S$  calculated with  $g^0$  and  $S^{\text{exp}}$  denotes the value derived from the experimental spectrum. The deviations of the one-particle constants  $g^0$  from the experimental ones are practically fully arisen due to the correlation effects. In table 1 the experimental ( $S^{\text{exp}}$ ) and theoretical ( $S^{\text{th}}$ ) values of the  $S$  parameter are presented for the molecules of CH, HF:  $S^0$  is the value without accounting for the correlation and reorganization corrections [2];  $S^{(b)}$  – the values of the parameter with accounting correlation and reorganization corrections within the simple (non-optimized) GF-DFT version [5] and the present work results (see [1-5] and Refs. therein).

Table 1.  
**The experimental ( $S^{\text{exp}}$ ) and theoretical ( $S^{\text{th}}$ ) values of the  $S$  parameter are presented for different molecules (CH, HF):  $S^0$  is the value without accounting correlation and reorganization corrections;  $S^{(b)}$  – the combined GF-DFT method (b).**

Molecule	S	$1\pi$	$3\sigma$
CH	$S^0$	0.22	0.105
	$S^{(b)}$	0.27	0.1134
	$S^{\text{(th-this work)}}$	0.38	0.120
HF	$S^0$	0.126	1.900
	$S^{(b)}$	0.192	2.053
	$S^{\text{(th-this work)}}$	0.313	2.115
	$S^{\text{(exp)}}$	0.35	2.13

It is interesting to list the similar data for the CO molecule:  $S^{\text{exp}}(1\pi)=2.30$ ;  $S^{\text{exp}}(4\sigma)=0.27$ ;  $S^{\text{exp}}(5\sigma)=0.04$ . It should be noted that more sophisticated calculation by Cederbaum et al [2] gives the theoretical value  $S(4,5\sigma)$ , which is practically identical to the experimental values, however the value  $S(1\pi)=2.59$  is in some degree different from  $S^{\text{exp}}$ . The similar our data are as follows:  $S^{\text{th}}(1\pi)=2.32$ ;  $S^{\text{th}}(4\sigma)=0.268$ ;  $S^{\text{th}}(5\sigma)=0.041$ . Note that our data are in physically reasonable agreement with the experimental data. It is interesting to present the data on the ionization potentials of the hydrogen fluoride (say, the ion state  $^2\Pi$ ): the experimental value (16.01 eV), the Koopmans' theorem (17.79 eV), the Hartree-Fock approximation (15.6 eV), the equations-of-motion approach (15.87 eV), this approach with accounting for correlation and reorganization corrections (15.97 eV). This results confirms the result [1-3] that the correlation and reorganization effects are the important corrections to Koopmans' theorem for this specific ionization potential. The most important aspect of all consideration is connected the principal possibility to reproduce diatomic spectra by applying a one-particle theory with accurate accounting for the correlation and reorganization effects. The hybrid DFT-GF theoretical approach can be prospectively used for quantitative treating photoelectron spectra of more complicated diatomic molecules.

## References

- [1]. Glushkov, A. V. *Relativistic quantum theory. Quantum mechanics of atomic systems*. Odessa: Astroprint, **2008**.
- [2]. Köppel, H.; Domcke, W.; Cederbaum, L. S. Green's function method in quantum chemistry. *Adv. Chem. Phys.* **1984**, *57*, 59-132.
- [3]. Smith W. D., Chen T. T, Simons J., Theoretical studies of molecular ions. Vertical ionization potentials of hydrogen fluoride. *J. Chem. Phys.* **1974**, *61*, 2670-2674.
- [4]. Fedchuk, A. P.; Glushkov, A. V.; Lepikh, Ya. I.; Loboda, A. V.; Lopatkin, Yu. M.; Svina-renko, A. A. The Green's functions and density functional approach to vibrational structure in the photoelectron spectra of carbon

- oxide molecule. *Photoelectronics*. **2010**, *19*, 115-120.
- [5]. Glushkov, A. V.; Buyadzhi, V. V.; Kvasikova, A. S.; Ignatenko, A. V.; Kuznetsova, A. A.; Prepelitsa, G. P.; Ternovsky, V. B. Non-Linear Chaotic Dynamics of Quantum Systems: Molecules in an Electromagnetic Field and Laser Systems. In: *Quantum Systems in Physics, Chemistry, and Biology*; Springer: Cham, **2017**, *30*, 169-180.
- [6]. Glushkov, A. V. Quasiparticle approach in the density functional theory under finite temperatures and dynamics of effective Bose – condensate. *Ukr. Phys. Journ.* **1993**, *38*, 152-157.
- [7]. Glushkov, A. V. An universal quasiparticle energy functional in a density functional theory for relativistic atom. *Optics and Spectr.* **1989**, *66*, 31-36.
- [8]. Glushkov, A.; Malinovskaya, S.; Sukharev, D.; Khetselius, O.; Loboda, A.; Lovett, L. Green's function method in quantum chemistry: New numerical algorithm for the Dirac equation with complex energy and Fermi-model nuclear potential. *Int. J. Quant. Chem.* **2009**, *109*, 1717-1727.
- [9]. Glushkov, A. V.; Malinovskaya, S. V.; Gurnitskaya, E. P.; Khetselius, O. Yu.; Dubrovskaya Yu. V. Consistent quantum theory of recoil induced excitation and ionization in atoms during capture of neutron. *J. Phys. Conf. Ser.* **2006**, *35*, 425-430.
- [10]. Glushkov, A.; Loboda, A.; Gurnitskaya, E.; Svinarenko, A. QED theory of radiation emission and absorption lines for atoms in a strong laser field. *Phys. Scripta*. **2009**, *T135*, 014022.
- [11]. Glushkov, A. V.; Khetselius, O. Y.; Svinarenko, A. A. Relativistic theory of cooperative muon- $\gamma$ -nuclear processes: Negative muon capture and metastable nucleus discharge. *Advances in the Theory of Quantum Systems in Chemistry and Physics, Series: Progress in Theor. Chem. and Phys.*; Hoggan, P., Brändas, E., Maruani, J., Delgado-Barrio, G., Piecuch, P., Eds.; Springer: Cham, **2012**; Vol. 22, pp 51-68.
- [12]. Glushkov, A. V.; Malinovskaya, S. V. Cooperative laser nuclear processes: border lines effects. *New projects and new lines of research in nuclear physics*. Fazio, G., Hanappe, F., Eds.; World Scientific: Singapore, **2003**; pp 242-250.
- [13]. Glushkov, A.; Khetselius, O.; Svinarenko, A.; Buyadzhi, V. *Spectroscopy of autoionization states of heavy atoms and multiply charged ions*. Odessa: TEC, **2015**.
- [14]. Khetselius, O. Y. Relativistic Energy Approach to Cooperative Electron- $\gamma$ -Nuclear Processes: NEET Effect. *Quantum Systems in Chemistry and Physics*; Springer: Dordrecht, **2012**; Vol. 26, pp 217-229.
- [15]. Khetselius, O. Yu. *Hyperfine structure of atomic spectra*. Astroprint: Odessa, **2008**.
- [16]. Khetselius, O. Yu. Relativistic perturbation theory calculation of the hyperfine structure parameters for some heavy-element isotopes. *Int. Journ. Quant. Chem.* **2009**, *109*, 3330-3335.
- [17]. Khetselius, O. Yu. Hyperfine structure of radium. *Photoelectronics*. **2005**, *14*, 83-85.
- [18]. Khetselius, O. Yu. Spectroscopy of cooperative electron-gamma-nuclear processes in heavy atoms: NEET effect. *J. Phys. Conf. Ser.* **2012**, *397*, 012012.
- [19]. Glushkov, A. V.; Malinovskaya, S. V.; Loboda, A. V.; Shpinareva, I. M.; Gurnitskaya, E. P.; Korchevsky, D. A. Diagnostics of the collisionally pumped plasma and search of the optimal plasma parameters of x-ray lasing: calculation of electron-collision strengths and rate coefficients for Ne-like plasma. *J. Phys.: Conf. Ser.* **2005**, *11*, 188-198.
- [20]. Khetselius, O. Yu. *Quantum structure of electroweak interaction in heavy finite Fermi-systems*. Astroprint: Odessa, **2011**.
- [21]. Glushkov, A. V.; Kondratenko, P. A.; Lepikh, Ya. I.; Fedchuk, A. P.; Svinarenko, A. A.; Lovett L. Electrodynamical and quantum - chemical approaches to modelling the electrochemical and catalytic processes on metals, metal alloys and semiconductors. *Int. J. Quant. Chem.* **2009**, *109*, 3473-3481.
- [22]. Glushkov, A. V.; Khetselius, O.; Gurnitskaya, E.; Loboda, A.; Sukharev, D. Relativistic quantum chemistry of heavy ions and hadronic atomic systems: spectra and ener-

- gy shifts. *AIP Conference Proc.* **2009**, 1102, 168-171.
- [23]. Florko, T. A., Loboda, A. V.; Svinarenko, A. A. Sensing forbidden transitions in spectra of some heavy atoms and multicharged ions: new theoretical scheme. *Sensor Electr. and Microsyst. Techn.* **2009**, Issue 3, 10-15.
- [24]. Buyadzhi, V.; Glushkov, A.; Mansarliysky, V.; Ignatenko, A.; Svinarenko, A. Spectroscopy of atoms in a strong laser field: New method to sensing AC Stark effect, multiphoton resonances parameters and ionization cross-section. *Sensor Electr. and Microsyst. Techn.* **2015**, 12(4), 27-36.
- [25]. Khetselius, O. Optimized relativistic many-body perturbation theory calculation of wavelengths and oscillator strengths for li-like multicharged ions. *Adv. Quant. Chem.* (Elsevier). **2018**, 78, doi. org/10. 1016/bs. aiq. 2018. 06. 001.
- [26]. *The Fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State*; Gidopoulos, N. and Wilson, S. Eds.; Springer: Berlin, **2004**; Vol. 14.

Стаття надійшла до редакції 17.09.2018 р.

PACS 33.20.-t; UDC 539.186

DOI <http://dx.doi.org/10.18524/1815-7459.2018.4.150505>

## PHOTOELECTRON SPECTROSCOPY OF DIATOMIC MOLECULES: HYBRID DENSITY FUNCTIONAL AND GREEN'S FUNCTIONS APPROACH TO SENSING MOLECULAR CONSTANTS

*A. V. Ignatenko, A. V. Glushkov, O. Yu. Khetselius, Yu. Ya. Bunyakova, A. A. Svinarenko*

Odessa State Environmental University, 15, Lvovskaya str., Odessa, 65016, Ukraine  
E-mail: [ignatenkoav13@gmail.com](mailto:ignatenkoav13@gmail.com)

### Summary

The aim of the work is to develop and present a new effective approach to analysis and calculation of the photoelectron spectra of diatomic molecules, vibrational structure characteristics and at whole molecular spectral constants.

It is developed the optimized version of the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach to quantitative treating the diatomic photoelectron spectra and molecular constants. The Fermi-liquid quasiparticle version of the density functional theory is 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 leads to significant simplification of the calculation and increasing an accuracy of theoretical prediction that is confirmed by computing the molecular spectral parameters for the molecules of CH, CO, HF etc.

**Keywords:** photoelectron spectra of molecules, new hybrid approach, Green's functions, density functional theory



**ФОТОЕЛЕКТРОННА СПЕКТРОСКОПІЯ ДВОАТОМНИХ МОЛЕКУЛ:  
ГІБРИДНИЙ МЕТОД ФУНКЦІОНАЛУ ГУСТИНИ ТА ФУНКЦІЙ ГРІНА У  
ВИЗНАЧЕННІ МОЛЕКУЛЯРНИХ КОНСТАНТ**

*Г. В. Ігнатенко, О. В. Глушков, О. Ю. Хецеліус, Ю. Я. Бунякова, А. А. Свинаренко*

Одеський державний екологічний університет, Львівська 15, 65016, Одеса

E-mail: [ignatenkoav13@gmail.com](mailto:ignatenkoav13@gmail.com)

**Реферат**

Метою роботи є розробка та представлення нового ефективного підходу до аналізу та розрахунку фотоелектронних спектрів двоатомних молекул, характеристик коливальної структури спектру і в цілому молекулярних спектральних констант.

Розвинута оптимізована версія гібридної комбінованої теорії функціоналу густини (DFT) і методу функцій Гріна (ГФ) для кількісного опису фотоелектронних спектрів двоатомних молекул та молекулярних констант. Новий гібридний підхід суттєво базується на фермірідинній квазічастинній версії теорії функціоналу густини. Густина стану, яка описує коливальну структуру в фотоелектронних спектрах, визначається з використанням комбінованого DFT-GF підходу та фізично розумно апроксимується за допомогою тільки першого порядку констант зв'язку в оптимізованому одноквазічастинковому наближенні.

Використання комбінованого DFT-GF підходу призводить до значного спрощення молекулярних обчислень та збільшення точності теоретичного прогнозування, що повністю підтверджується відповідними обчисленнями спектральних параметрів для молекул CH, CO, HF тощо.

**Ключові слова:** фотоелектронний спектр молекул, новий гібридний підхід, метод функцій Гріна, теорія функціоналу густини