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ADVANCED GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRON SPECTRA OF DIATOMIC MOLECULE

The advanced combined theoretical approach to vibrational structure in photoelectron spectra of diatomic molecules, which is based on the density functional theory (DFT) and the Green's-functions approach, is used for quantitative treating the diatomic photoelectron spectra. The density of states, which describe the vibrational structure in photoelectron spectra, is defined with the use of combined DFT-Green's-functions approach and is well approximated by using only the first order coupling constants in the one-particle approximation. Using the DFT theory leads to significant simplification of the calculation.

1. Introduction

The Green's method is very well known in a quantum theory of field, quantum theory of solids. Naturally, an attractive idea was to use it in the molecular theory. Regarding a problem of description of the vibrational structure in photoelectron spectra of molecules, it is easily understand that this approach has great perspective (c.f.[1-51]). One could note that the experimental photoelectron (PE) spectra usually show a pronounced vibrational structure. Usually the electronic Green's function is defined for fixed position of the nuclei. As result, only vertical ionization potentials (V.I.P.'s) can be calculated [11,2,11,12]. 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. Naturally, the Franck-Condon factors are functions of the derivatives of the difference between the potential curves of the initial and final states with respect to the normal coordinates. To avoid the difficulty and to gain additional information about the ionization process, the Green's functions approach has

been extended to include the vibrational effects in the photoelectron spectra. Nevertheless, there are well known great difficulties of the correct interpretation of the photoelectron spectra for any molecules.

Here we present the advanced combined theoretical approach to vibrational structure in photoelectron spectra of diatomic molecules and use it for effective quantitative treating the diatomics photoelectron spectra. The advanced approach is based on the Green's function method (Cederbaum-Domske version) [11,12], Fermi-liquid DFT formalism [1-8] and use of the novel effective density functionals (see also [13-16]). As usually (see Refs. [2,4,11]), the density of states, which describe the vibrational structure in molecular photoelectron spectra, is calculated with the help of combined DFT-Green's-functions approach. In addition to exact solution of one-bode problem different approaches to calculate reorganization and many-body effects are presented. 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. Method: Density of states in one-body and many-body solution

As usually (see details in refs. [1-12]), 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:

$$N_k(\epsilon) = (1/2\pi\hbar)\int dt e^{ih^{-1}\epsilon t}\langle\psi_0|a_k^t(0)a_k(t)|\psi_0\rangle, \quad (1)$$

where $|\Psi_0\rangle$ is the exact ground state wave function of the reference molecule and $a_k(t)$ is an electron destruction operator, both in the Heisenberg picture. For particle attachment the quantity of interest is the density of unoccupied states:

$$N_k(\epsilon) = (1/2\pi\hbar)\int dt e^{ih^{-1}\epsilon t}\langle\psi_0|a_k(t)a_k^t(0)|\psi_0\rangle \quad (2)$$

Usually in order to calculate the value (1) states for photon absorption one should express the Hamiltonian of the molecule in the second quantization formalism. The Hamiltonian is as follows:

$$H = T_E(\partial/\partial x) + T_N(\partial/\partial X) + U_E(x) + \\ + U_N(X) + U_{\mathbb{N}}(x,X) \quad (3)$$

where T_E and T_N are the kinetic energy operators for electrons and nuclei, and U represents the interaction; U_E represents the Coulomb interaction between electrons, etc; x (X) denotes electron (nuclear) coordinates. 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 ϕ_i ($\in_i (R)$ 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 [2,11]:

$$H = H_E + H_N + H_{EN}^{(1)} + H_{EN}^{(2)}, \quad (4)$$

$$H_E = \sum_i \overset{\epsilon}{V_i}(R_0)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R_0)a_i^t a_j^t a_l a_k - \\ - \sum_{i,j}\sum_{k\in f}[V_{ikjk}(R_0) - V_{ikkj}(R_0)]a_i^t a_j$$

$$H_N = \hbar\sum_{s=1}^{M}\omega_s(b_s^t b_s + \frac{1}{2}),$$

$$H_{EN}^{(1)} = 2^{-1/2}\sum_{s=1}^{M}\left(\frac{\partial V_i}{\partial Q_s}\right)_0 (b_s + b_s^t)[a_i^t a_i - n_i] + \\ + \frac{1}{4}\sum_i\sum_{s,s'=1}^{M}\left(\frac{\partial^2 V_i}{\partial Q_s\partial Q_{s'}}\right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t)[a_i^t a_i -$$

$$H_{EN}^{(2)} = 2^{-3/2}\sum\sum_{s=1}^{M}\left(\frac{\partial V_{ijkl}}{\partial Q_s}\right)_0 (b_s + b_s^t)[\delta v_1 a_i^t a_j^t a_k \\ + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t] +$$

$$+ \frac{1}{8}\sum\sum_{s,s'=1}^{M}\left(\frac{\partial^2 V_{ijkl}}{\partial Q_s\partial Q_{s''}}\right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t)\cdot \\ [\delta v_1 a_i^t a_j^t a_k + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t]$$

with n_i=1 (0), $i\in f$ ($i\in f$), $\delta\sigma_f$=1 (0) , $(ijkl)\in\sigma_{f}$ where the index set v_1 means that at least ϕ_k and ϕ_l or ϕ_i and ϕ_j are unoccupied, v_2 that at most one of the orbitals is unoccupied, and v_3 that ϕ_k and ϕ_j or ϕ_l and ϕ_j are unoccupied. Here for simplicity all terms leading to anharmonicities are neglected. The ω_s are the HF frequencies; b_s, b_s^t are destruction and creation operators for vibrational quanta as

$$Q_s = (1/\sqrt{2})(b_s + b_s^t)$$

$$\partial/\partial Q_s = (1/\sqrt{2})(b_s - b_s^t). \quad (5)$$

The interpretation of the above Hamiltonian and an exact solution of the one-body HF problem is given in refs. [1,2,11,12]. The HF-single-particle component H_0 of the Hamiltonian (4) is as follows:

$$H_0 = \sum_i \varepsilon^{\circ}{}_i(R_0) a_i^t a_i + \sum_{s=1}^{M} \hbar\omega_s(b_s^t b_s + \frac{1}{2}) +$$

$$\sum_{s=1}^{M} \sum_i 2^{-1/2} \left(\frac{\partial^{\circ} V_i}{\partial Q_s}\right) [a_i^t a_i - n_i] (b_s + b_s^t)_0 +$$

$$+ \sum_{s,s'=1} \sum_i \frac{1}{4} \left(\frac{\partial^{2\,\circ} V_i}{\partial Q_s \partial Q_{s'}}\right)_0 [a_i^t a_i - n_i] \cdot$$

$$\cdot (b_s + b_s^t)(b_{s'} + b_{s'}^t) \tag{6}$$

Correspondingly in the one-particle picture the density of occupied states is given by

$$N_k^0(^\circ) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(^\circ - {}^\circ{}_k)t} \langle 0| \, e^{\pm i\hbar^{-1}\tilde{H}_{0'}} |0\rangle, \tag{7}$$

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

$$+ \sum_{s,s'=1}^{M} \gamma_s^k{}_{,'} (b_s + b_s^t)(b_{s'} + b_{s'}^t) \tag{8}$$

$$g_s^i = \pm\frac{1}{\sqrt{2}} \left(\frac{\partial^{\circ}{}_i}{\partial Q_s}\right)_0, \quad \gamma_s^i{}_{,'} = \pm\frac{1}{4} \left(\frac{\partial^{2\,\circ}{}_i}{\partial Q_s \partial Q_{s'}}\right)_0 \cdot \tag{9}$$

Introducing new operators

$$c_s = \sum_{l=1}^{M} (\lambda_1^s b_l + \lambda_2^s b_l^t) \tag{10}$$

with real coefficients λ_1^s, λ_2^s, defined in such a way that $\tilde{H}_0$ in new operators is

$$\tilde{H}_0 = \sum_{s=1}^{M} \hbar\hat{\omega}_s c_s^t c_s + \sum_{s=1}^{M} \hat{g}_s (c_s + c_s^t) + k. \tag{11}$$

eq. (7) is as follows:

$$N_k^0(^\circ) = \sum_{n_1 \cdots n_M} |\langle \hat{n}| U |0\rangle|^2 \delta(^\circ - {}^\circ{}_k \pm \Delta^{\circ}{}_k \pm n \cdot \hbar\hat{\omega}) \tag{12}$$

where δ function in (12) naturally contains the information about adiabatic ionization potential and the spacing of the vibrational peaks; $|\langle \hat{n}| U |0\rangle|^2$ is the well-known Franck-Condon factor. In a diagrammatic method to get function $N_k(^\circ)$ one should calculate the GF $G_k{}_{,'}(^\circ)$ first [1,2,11,12]:

$$G_{k{}_{,'}}(^\circ) = -i\hbar^{-1} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}t} \langle\psi_0| \dot{O}\{ a_k(t)a_k^t(0) \} |\psi_0\rangle \tag{13}$$

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

$$\pi N_k(^\circ) = a \operatorname{Im} G_k (^\circ - i\eta), \quad a = -\operatorname{sign}^{\circ}{}_k. \tag{14}$$

Choosing the unperturbed Hamiltonian H_0 to be $H_0 = \sum {}^\circ{}_i a_i^t a_i + H_N$ one finds the GF. In the known approximation GF is as follows:

$$G_{kk'}^{\theta}(t) = \pm\delta_{kk'} i \exp\left[-\hbar^{-1}(\varepsilon_k \mp \Delta\varepsilon)t\right] \cdot$$

$$\cdot \sum_n |\langle \hat{n}_k| U_k |0\rangle|^2 \exp(\pm \hbar_k \cdot \hat{\omega}_k t) \tag{15}$$

The direct method for calculation of $N_k(\in)$ 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 $N_k(\in)$. The zeros of the functions

$$D_k(\in) \in -\left[\in^p +\Sigma(\in)\right]_k, \tag{16}$$

where $(\in^p +\Sigma)_k$ 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 [2,11,12]:

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

$$F_k = \Sigma_k \left(-(V.I.P.)_k\right) \approx \frac{1}{1 - \partial\Sigma_k (\in_k)/\partial_\in} \Sigma_k (\in_k). \tag{17}$$

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 δQ_s, and new coupling constants are then:

$$g_l = \pm(1/\sqrt{2})[\partial(\in_k +F_k)/\partial Q_l]_0 \tag{18}$$

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

The coupling constants g_l and $y_{ll'}$ are calculated by the well-known perturbation expansion of the

self-energy part using the Hamiltonian H_{EN} of Eq. (3). In second order one obtains:

$$\sum_{k}^{(2)}(\in) = \sum_{\substack{i,j \\ s \notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s \notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j}$$

(19)

and the coupling constant g_p are written as

$$g_l \approx \pm \frac{1}{\sqrt{2}} \frac{\partial \in_k}{\partial Q_l} \frac{1 + q_k (\partial / \partial \in) \sum_k [-(V.I.P.)_k]}{1 - (\partial / \partial \in) \sum_k [-(V.I.P.)_k]},$$

$$q_k = A / B$$

$$A = \sum \frac{(V_{ksij} - V_{ksji})^2}{[-(V.I.P.)_k + \in_s - \in_i - \in_j]^2} \bullet$$

$$\bullet \left[\frac{\partial \in_s}{\partial Q_l} - \frac{\partial \in_i}{\partial Q_l} - \frac{\partial \in_j}{\partial Q_l} \right]$$

$$B = \frac{\partial \in_k}{\partial Q_l} \sum \frac{(V_{ksij} - V_{ksji})^2}{[-(V.I.P.)_k + \in_s - \in_i - \in_j]^2}$$

(20)

It is suitable to use further the pole strength of the corresponding GF:

$$\rho_k = \left\{ 1 - \frac{\partial}{\partial \in} \sum_k [-(V.I.P)_k] \right\}^{-1}; 1 \geq \rho_k \geq 0,$$

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

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

(21)

Below we give the DFT definition of the pole strength corresponding to V. I. P.'s and confirm the earlier data [11-15]: $p_k \approx 0,8$-$0,95$. The coupling constant is:

$$\gamma_{ll} = \gamma_l^0 \left(\frac{g_l}{g_l^0} \right) + \frac{1}{4} \sqrt{2} g_l^0 \frac{\partial}{\partial Q_l} \left(\frac{g_l}{g_l^0} \right)$$

(22)

3. Fermi-liquid quasiparticle density functional theory

Further we consider the quasiparticle Fermi-liquid version of the DFT, following to refs. [1-3,8,17]. 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:

$$\nu_0(r) = \sum_\lambda n_\lambda |\Phi_\lambda(r)|^2,$$

$$\nu_1(r) = \sum_\lambda n_\lambda |\nabla \Phi_\lambda(r)|^2,$$

(23)

$$\nu_2(r) = \sum_\lambda n_\lambda [\Phi_\lambda^* \Phi_\lambda - \Phi_\lambda^* \Phi_\lambda]$$

The densities ν_0 and ν_1 are similar to the HF electron density and kinetical energy density correspondingly; the density ν_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 Σ. 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 a free Lagrangian L_q^0 has a standard form:

$$L_q^0 = \int d \sum_\lambda n_\lambda \Phi_\lambda^* (i\partial / \partial t - \varepsilon_p) \Phi_\lambda,$$

(24)

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 Σ :

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

(25)

where β_{ik} are some constants (look below), F is an effective potential of the exchange-correlation interaction. The Coulomb interaction part L_K looks as follows:

$$L_K = -\frac{1}{2} \int [1 - \sum_2(r_1)] \nu_0(r_1) [1 - \\ - \sum_2(r_2)] \nu_0(r_2) / |r_1 - r_2| dr_1 dr_2$$

(26)

where $\Sigma_2 = \partial \Sigma / \partial \varepsilon$. In the local density approximation the potential F can be expressed through the exchange-correlation pseudo-potential V_{xc} as follows:

$$F(r_1, r_2) = \delta V_{xc} / \delta \nu_0 \cdot \delta(r_1 - r_2).$$

(27)

Further, one can get the following expressions for $\Sigma_i = -\delta L_q^{int} / \delta \nu_i$:, in particular:

$$\Sigma_1 = \beta_{01}\delta V_{XC} / \delta v_0 \cdot v_0 + \beta_{12}\delta V_{XC} / \delta v_0 \cdot v_2 + \\ + \beta_{11}\delta V_{XC} / \delta v_0 \cdot v_1$$

$$\Sigma_2 = \beta_{02}\delta V_{XC} / \delta v_0 \cdot v_0 + \beta_{12}\delta V_{XC} / \delta v_0 \cdot v_1 + \\ + \beta_{22}\delta V_{XC} / \delta v_0 \cdot v_2 \qquad (28)$$

Here V_K is the Coulomb term, Σ_0^{α} is the exchange term. Using the known canonical relationship, one can derive the quasiparticle Hamiltonian, which is corresponding to L_q. Further constants β_{ik} should be defined. In some degree they have the same essence as the similar constants in the well-known Landau Fermi-liquid theory and the Migdal finite Fermi-systems theory. Regarding universality of β_{ik}, indeed, as we know now, the total universality of the constants in the last theories is absent, though a range of its changing is quite small [2,17]. The value of β_{00} is dependent on definition of V_{xc}. If as V_{xc} it is used one of the DFT exchange-correlation potentials from, then without losing a community of statement, $\beta_{00}=1$. The constant β_{02} can be in principle calculated by analytical way, but it is very useful to remember its connection with a spectroscopic factor F_{sp} of the system [18]:

$$F_{sp} = \left\{ 1 - \frac{\partial}{\partial \in} \sum_k \left[-(V.I.P)_k \right] \right\} \qquad (29)$$

The terms $\partial \sum / \partial \varepsilon$ and $\sum_2$ is directly linked [2,17]. In the terms of the Green function method expression (7) is in fact corresponding to the pole strength of the Green's function [2]. The new element of an approach can be connected with using the DFT correlation functional of the Lee-Yang-Parr (LYP) (look details in ref. [13-16]).

3. Results and conclusions

As illustration, we choose the diatomic molecule of N_2 for application of the combined Green's function method and quasiparticle DFT approach. The nitrogen molecule has been naturally discussed in many papers. The valence V. I. P. 's of N_2 have been calculated [1,13,14,24] by the method of Green's functions and therefore the pole strengths p_k are known and the mean values q_k can be estimated. It should be reminded that the N_2

molecule is the classical example where the known Koopmans' theorem even fails in reproducing the sequence of the V. I. P. 's in the PE spectrum. From the HF calculation of Cade *et al.*[24] one finds that including reorganization the V. I. P. 's assigned by σ_g and σ_u improve while for π V. I. P. the good agreement between the Koopmans value and the experimental one is lost, leading to the same sequence as given by Koopmans' theorem. In Table 1 the experimental V. I. P. 's (a), the one-particle HF energies (b), the V. I. P. 's calculated by Koopmans' theorem plus the contribution of reorganization (c), the V. I. P. 's calculated with Green's functions method (d), the combined Green functions and DFT approach (e), the similar our results (f).

Table 1

The experimental and calculated V. I. P.'s (in eV) of N_2. R_k is the contribution of reorganization; p_k stands for pole strength.

Orbital	Exptl[a] V.I.P.'s	$-\in_k^b$	$-(\in_k + R_k)^c$
$3\sigma_g$	15,60	17,36	16,01
$1\pi_u$	16,98	17,10	15,67
$2\sigma_u$	18,78	20,92	19,93
Orbital	Calc[d] V.I.P.'s	Calc[e] V.I.P.'s	Calc[f] V.I.P. ρ_k^e
$3\sigma_g$	15,50	15,52	15,58
$1\pi_u$	16,83	16,85	16,96
$2\sigma_u$	18,59	18,63	18,76

The important point of all consideration is connected the principal possibility to reproduce diatomic spectra by applying a one-particle theory with account of the correlation and reorganization effects. The combined theoretical approach, which is based on the quasiparticle DFT with using

correct DF and the Green's-functions approach can be prospectively used for quantitative treating the diatomic photoelectron spectra. It is very important that the computational complexity of the combined approach is significantly lower in comparison with original version of the Green's-functions method.

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ADVANCED GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRON SPECTRA OF DIATOMIC MOLECULE

Summary

The advanced combined theoretical approach to vibrational structure in photoelectron spectra of molecules, which is based on the density functional theory (DFT) and the Green's-functions (GF) approach, is used for quantitative treating the diatomics photoelectron spectra. The density of states, which describe the vibrational structure in photoelectron spectra, is defined with the use of combined 'density functional-Green's functions' approach and is well approximated by using only the first order coupling constants in the one-particle approximation. Using the DFT theory leads to significant simplification of the molecular calculations.

Key words: photoelectron spectra of molecules, Green's functions, density functional theory

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ОБОБЩЕННЫЙ МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ В ОПРЕДЕЛЕНИИ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ ФОТОЭЛЕКТРОННОГО СПЕКТРА ДВУХАТОМНЫХ МОЛЕКУЛ

Резюме

Усовершенствованный комбинированный теоретический метод описания вибрационной структуры для фотоэлектронных спектров молекул, основанный на методе функций Грина и теории функционала плотности, применен к количественному описанию фотоэлектронного спектра двухатомных молекул. Плотность состояний, которые описывают колебательную структуру в фотоэлектронных спектрах, определяется с использованием комбинированного подхода (метод функционала плотности и функций Грина) и хорошо аппроксимируется с использованием только первого порядка констант связи в одноквазичастичном приближении. Использование теории функционала плотности приводит к значительному упрощению молекулярных расчетов.

Ключевые слова: фотоэлектронный спектр молекул, метод функций Грина, теория функционала плотности

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УДОСКОНАЛЕНИЙ МЕТОД ФУНКЦІЙ ГРІНА І ФУНКЦІОНАЛУ ГУСТИНИ У ВИЗНАЧЕННІ ВІБРАЦІЙНОЇ СТРУКТУРИ ФОТОЕЛЕКТРОННОГО СПЕКТРУ ДВОАТОМНИХ МОЛЕКУЛ

Резюме

Удосконалений комбінований теоретичний метод опису вібраційної структури для фотоелектронних спектрів молекул, який базується на методі функцій Гріна і теорії функціоналу густини , застосовано до кількісного опису фотоелектронного спектру двоатомних молекул. Густина станів, які описують коливальну структуру у фотоелектронних спектрах, визначається з використанням комбінованого Гріна підходу (метод функціоналу густини і функцій Гріна) та добре апроксимується з використанням тільки першого порядку констант зв'язку в одноквазі-частинковому наближенні. Використання теорії функціоналу густини призводить до значного спрощення молекулярних розрахунків.

Ключові слова: фотоелектронний спектр молекул, метод функцій Гріна, теорія функціонала густини