

I. I. Mechnikov Odessa National University
 Odessa State Environmental University,
 Sumy National University
 e-mail: dirac13@mail.ru

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

The combined theoretical approach to vibrational structure in photoelectron spectra (PES) of molecules, which is based on the density functional theory (DFT) and the Green's-functions (GF) approach, is used for quantitative treating the carbon oxide molecule PES.

INTRODUCTION

The 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. [1–15]). The experimental PES spectra of molecules usually show a pronounced vibrational structure [5–6]. 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 [11] 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 [16,17] or from the wave-function world the simplest correlated model MBPT are preferred [2,8,10]. Indeed, in the last decades DFT theory became by a great, quickly developing field of the modern computational chemistry of molecules. Here the combined theoretical approach [12–15] to vibrational structure in PES of molecules, which is based on the DFT and the GF approach, is used for quantitative treating the carbon oxide molecule. The density of states, which describe the vibrational structure in PES, is calculated with using combined DFT-GF approach. It is important that calculation procedure is significantly simplified with using DFT formalism. This simplification allowed to get the first important results in a laser-electron- γ nuclear spectroscopy of molecules [14], namely, results on the electron-vibration-rotation- γ nuclear satellite lines.

The density of states in one-body and many-body problem.

Quasiparticle Fermi-liquid density functional theory

As usually (see details in refs. [2,8,11,14]), 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:

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

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:

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

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:

$$H = T_E(\partial/\partial x) + T_N(\partial/\partial X) + U_{EE}(x) + U_{NN}(X) + U_{EN}(x, X), \quad (3)$$

where T_E and T_N are the kinetic energy operators for electrons and nuclei, and U represents the interaction; U_{EE} represents the Coulomb interaction between electrons, etc; $x(X)$ denotes electron (nuclear) coordinates. As usually, introducing a field operator $\Psi(R, \theta, x) = \sum \phi_i(x, R, \theta) a_i(R, \theta)$ 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 [11,15]:

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

$$H_E = \sum_i \epsilon_i(R_0) a_i^\dagger a_i + \frac{1}{2} \sum_{ijkl} V_{ijkl}(R_0) a_i^\dagger a_j^\dagger a_l a_k - \sum_{i,j} \sum_{k \in f} [V_{ijk}(R_0) - V_{ikk}(R_0)] a_i^\dagger a_j,$$

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

$$\begin{aligned}
H_{EN}^{(1)} &= 2^{-1/2} \sum_{s=1}^M \left(\frac{\partial^o}{\partial Q_s} \right)_0 (b_s + b'_s) [a'_i a_i - n_i] + \\
&+ \frac{1}{4} \sum_i \sum_{s,s'=1}^M \left(\frac{\partial^2 o}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b'_s)(b_{s'} + b'_{s'}) [a'_i a_i - n_i], \\
H_{EN}^{(2)} &= 2^{-3/2} \sum_{s=1}^M \sum_{s'=1}^M \left(\frac{\partial V_{ijkl}}{\partial Q_s} \right)_0 (b_s + b'_s) \times \\
&\times [\delta v_1 a'_i a'_j a_k + \delta v_2 a_i a_k a'_i a'_j + 2\delta v_3 a'_i a'_j a_k a_i] + \\
&\frac{1}{8} \sum_{s,s'=1}^M \left(\frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b'_s) \times \\
&\times (b_{s'} + b'_{s'}) [\delta v_1 a'_i a'_j a_k + \delta v_2 a_i a_k a'_i a'_j + 2\delta v_3 a'_i a'_j a_k a_i],
\end{aligned}$$

with $n_i=1$ (0), $i \in f$ ($i \notin f$), $\delta \sigma_f=1$ (0), $(ijkl) \in \sigma_{f \rightarrow}$, 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_l or φ_i 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 are destruction and creation operators for vibrational quanta as

$$Q_s = (1/\sqrt{2})(b_s + b'_s), \quad \partial / \partial Q_s = (1/\sqrt{2})(b_s - b'_s) \quad (5)$$

The interpretation of the above Hamiltonian and an exact solution of the one-body HF problem is given in refs. [5,6]. The HF-single-particle component H_0 of the Hamiltonian (4) is as follows:

$$\begin{aligned}
H_0 &= \sum_i \epsilon_i (R_0) a'_i a_i + \sum_{s=1}^M \hbar \omega_s (b'_s b_s + \frac{1}{2}) + \\
&+ \sum_{s=1}^M \sum_i 2^{-1/2} \left(\frac{\partial^o}{\partial Q_s} \right) [a'_i a_i - n_i] (b_s + b'_s)_0 + \\
&+ \sum_{s,s'=1}^M \sum_i \frac{1}{4} \left(\frac{\partial^2 o}{\partial Q_s \partial Q_{s'}} \right) [a'_i a_i - n_i] (b_s + b'_s)(b_{s'} + b'_{s'}) \quad (6)
\end{aligned}$$

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

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(\epsilon - \epsilon_k)t} \langle 0 | e^{\pm i\hbar^{-1}\tilde{H}_0 t} | 0 \rangle, \quad (7)$$

$$\begin{aligned}
\tilde{H}_0 &= \sum_{s=1}^M \hbar \omega_s b'_s b_s + \sum_{s=1}^M g_s^k (b_s + b'_s) + \\
&+ \sum_{s,s'=1}^M \gamma_{ss'}^k (b_s + b'_s)(b_{s'} + b'_{s'}) \quad (8)
\end{aligned}$$

$$g_s^i = \pm \frac{1}{\sqrt{2}} \left(\frac{\partial^o}{\partial Q_s} \right), \quad \gamma_{ss'}^i = \pm \frac{1}{4} \left(\frac{\partial^2 o}{\partial Q_s \partial Q_{s'}} \right). \quad (9)$$

Introducing new operators

$$c_s = \sum_{l=1}^M (\lambda_1^{sl} b_l + \lambda_2^{sl} b'_l) \quad (10)$$

with real coefficients $\lambda_1^{sl}, \lambda_2^{sl}$, defined in such a way that \tilde{H}_0 in new operators is

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

eq. (7) is as follows:

$$\begin{aligned}
N_k^0(\epsilon) &= \sum_{n_1, \dots, n_M} | \langle \hat{n} | U | 0 \rangle |^2 \times \\
&\times \delta(\epsilon - \epsilon_k \pm \Delta \epsilon_k \pm n \cdot \hbar \hat{\omega}) \quad (12)
\end{aligned}$$

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 $N_k(\epsilon)$ one should calculate the GF $G_{kk'}(\epsilon)$ first [1,3,11,18]:

$$\begin{aligned}
G_{kk'}(\epsilon) &= -i\hbar^{-1} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}\epsilon t} \times \\
&\times \langle \psi_0 | T \{ a_k(t) a'_k(0) \} | \psi_0 \rangle \quad (13)
\end{aligned}$$

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

$$\pi N_k(\epsilon) = a \text{Im} G_{kk}(\epsilon - ai\eta), \quad a = -\text{sign} \epsilon_k. \quad (14)$$

Choosing the unperturbed Hamiltonian H_0 to be $H_0 = \sum \epsilon_i a'_i a_i + H_N$ one finds the GF. In the known approximation GF is as follows:

$$\begin{aligned}
G_{kk'}^{OB}(t) &= \pm \delta_{kk'} i \exp[-in^{-1}(\epsilon_k \mp \Delta \epsilon)t] \times \\
&\times \sum_n \langle \hat{n}_k | U_k | 0 \rangle^2 \exp(\pm i n_k \cdot \hat{\omega}_k t), \quad (15)
\end{aligned}$$

The corresponding Dyson-like equation ($\Sigma = \hat{O}$) is as follows:

$$G_{kk'}(\epsilon) = G_{kk'}^{OB}(\epsilon) + \sum_{kk''} G_{kk''}^{OB}(\epsilon) \Phi_{kk''} G_{k''k'}(\epsilon) \quad (16)$$

$$\begin{aligned}
\Phi_{kk'}(\epsilon) &= \sum_{\substack{i,j \in F \\ l \notin F}} \sum_{n_i, n_j, n_l} \frac{(V_{klj} - V_{klij}) V_{k'l'ij} U_{n_i} U_{n_j} U_{n_l}}{\epsilon + E_l - E_i - E_j} + \\
&+ \sum_{\substack{i,j \in F \\ l \notin F}} \sum_{n_i, n_j, n_l} \frac{(V_{klj} - V_{klij}) V_{k'l'ij} U_{n_i} U_{n_j} U_{n_l}}{\epsilon + E_l - E_i - E_j}
\end{aligned}$$

where $U_{n_i} = | \langle \hat{n}_i | U_i | 0 \rangle |^2$ and $E_i = \epsilon_i \mp \Delta \epsilon_i \mp \hbar \hat{n}_i \cdot \hat{\omega}_i$ (17)

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

$$D_k(\epsilon) = \epsilon - [\epsilon^{op} + \Sigma(\epsilon)]_k, \quad (18)$$

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 [11,13]:

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

$$F_k = \Sigma_{kk}(- (V.I.P.)_k) \approx \frac{1}{1 - \partial \Sigma_{kk}(\epsilon_k) / \partial \epsilon} \Sigma_{kk}(\epsilon_k). \quad (19)$$

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:

$$g_i = \pm (1/\sqrt{2}) \left[\partial(\epsilon_k + F_k) / \partial Q_i \right]_0 \quad (20)$$

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

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:

$$\sum_{kk}^{(2)}(\epsilon) = \sum_{\substack{i,j \\ s \notin F}} \frac{(V_{ksij} - V_{ksji}) V_{ksij}}{\epsilon + \epsilon_s - \epsilon_i - \epsilon_j} + \sum_{\substack{i,j \\ s \in F}} \frac{(V_{ksij} - V_{ksji}) V_{ksij}}{\epsilon + \epsilon_s - \epsilon_i - \epsilon_j} \quad (21)$$

and the coupling constant g_p can be written as

$$g_l \approx \pm \frac{1}{\sqrt{2}} \frac{\partial \epsilon_k}{\partial Q_l} \frac{1 + q_k (\partial / \partial \epsilon) \sum_{kk} [-(V.I.P.)_k]}{1 - (\partial / \partial \epsilon) \sum_{kk} [-(V.I.P.)_k]}, \quad (22)$$

$$q_k = \frac{\sum \frac{(V_{ksij} - V_{ksji})^2}{[-(V.I.P.)_k + \epsilon_s - \epsilon_i - \epsilon_j]^2} \left[\frac{\partial \epsilon_s}{\partial Q_l} - \frac{\partial \epsilon_i}{\partial Q_l} - \frac{\partial \epsilon_j}{\partial Q_l} \right]}{\frac{\partial \epsilon_k}{\partial Q_l} \sum \frac{(V_{ksij} - V_{ksji})^2}{[-(V.I.P.)_k + \epsilon_s - \epsilon_i - \epsilon_j]^2}} \quad (23)$$

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

$$\rho_k = \left\{ 1 - \frac{\partial}{\partial \epsilon} \sum_{kk} [-(V.I.P.)_k] \right\}^{-1}; 1 \geq \rho_k \geq 0, \quad (24)$$

$$g_l \approx g_l^0 [\rho_k + q_k (\rho_k - 1)], \quad g_l^0 = \pm 2^{-1/2} \partial \epsilon_k / \partial Q_l \quad (25)$$

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:

$$\gamma_{ll} = \gamma_{ll}^0 \left(\frac{g_l}{g_l^0} \right) + \frac{1}{4} \sqrt{2} g_l^0 \frac{\partial}{\partial Q_l} \left(\frac{g_l}{g_l^0} \right) \quad (26)$$

Further we consider the quasiparticle Fermi-liquid version of the DFT, following to refs. [18–20]. The master equation can be derived using an expansion for self-energy part Σ into set on degrees of x , $\epsilon - \epsilon_F$, $p^2 - p_F^2$ (here ϵ_F and p_F are the Fermi energy and pulse correspondingly):

$$[p^2 / 2 - \sum_{\alpha} Z_{\alpha} / r_{\alpha} + \sum_0(x) + p(\partial \Sigma / \partial p^2)] \Phi_{\lambda}(x) = (1 - \partial \Sigma / \partial \epsilon) \epsilon_{\lambda} \Phi_{\lambda}(x) \quad (27)$$

The functions Φ_{λ} in (27) are orthogonal with a weight $\rho_k^{-1} = a^{-1} = [1 - \partial \Sigma / \partial \epsilon]$. Now one can introduce wave functions of the quasiparticles $\phi_{\lambda} = a^{-1/2} \Phi_{\lambda}$, which are, as usually, orthogonal with weight 1. The equations (27) can be obtained on the basis of variational principle, if we start from a Lagrangian of a system L_q (DF). It should be defined as a functional of quasiparticle densities:

$$v_0(r) = \sum_{\lambda} n_{\lambda} |\Phi_{\lambda}(r)|^2,$$

$$v_1(r) = \sum_{\lambda} n_{\lambda} |\nabla \Phi_{\lambda}(r)|^2,$$

$$v_2(r) = \sum_{\lambda} n_{\lambda} [\Phi_{\lambda}^* \Phi_{\lambda} - \Phi_{\lambda}^* \Phi_{\lambda}],$$

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 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:

$$L_q^0 = \int dr \sum_{\lambda} n_{\lambda} \Phi_{\lambda}^* (i\partial / \partial t - \epsilon_p) \Phi_{\lambda}, \quad (28)$$

The interaction Lagrangian is defined in the form, which is characteristic for a standard (Kohn-Sham [16]) 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 :

$$L_q^{int} = L_K - \frac{1}{2} \sum_{i,k=0}^2 \int \beta_{ik} F(r_1, r_2) v_i(r_1) v_k(r_2) dr_1 dr_2 \quad (29)$$

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:

$$L_K = -\frac{1}{2} \int [1 - \sum_2(r_1)] v_0(r_1) [1 - \sum_2(r_2)] v_0(r_2) / |r_1 - r_2| dr_1 dr_2 \quad (30)$$

where $\Sigma_2 = \partial \Sigma / \partial \epsilon$. In the local density approximation the potential F can be expressed through the exchange-correlation pseudo-potential V_{xc} as follows [20]:

$$F(r_1, r_2) = \delta V_{xc} / \delta v_0 \delta(r_1 - r_2).$$

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

$$\begin{aligned} \Sigma_0 &= (1 - \Sigma_2) V_K + \Sigma_0^{\text{ex}} + \frac{1}{2} \beta_{00} \delta^2 V_{xc} / \delta v_0^2 v_0^2 + \\ &+ \beta_{00} \delta V_{xc} / \delta v_0 v_0 + \beta_{01} \delta V_{xc} / \delta v_0 v_1 + \\ &+ \beta_{01} \delta^2 V_{xc} / \delta v_0^2 \cdot v_0 v_1 + \beta_{02} \delta^2 V_{xc} / \delta v_0^2 \cdot v_0 v_2 + \\ &+ \beta_{02} \delta V_{xc} / \delta v_0 \cdot v_2 \end{aligned} \quad (31)$$

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

$$\Sigma_2 = \beta_{02} \delta V_{xc} / \delta v_0 \cdot v_0 + \beta_{12} \delta V_{xc} / \delta v_0 \cdot v_1 + \beta_{22} \delta V_{xc} / \delta v_0 \cdot v_2$$

Here V_K is the Coulomb term, Σ_0^{ex} is the exchange term. Using the known canonical relationship, one can derive the quasiparticle Hamiltonian, which is corresponding to L_q :

$$\begin{aligned} H_q &= H_q^0 + H_q^{int} = H_q^0 - L_K + \\ &+ \frac{1}{2} \beta_{00} \delta V_{xc} / \delta v_0 \cdot v_0^2 + \beta_{01} \delta V_{xc} / \delta v_0 \cdot v_0 \cdot v_1 + \\ &+ \frac{1}{2} \beta_{11} \delta V_{xc} / \delta v_0 \cdot v_1^2 - \frac{1}{2} \beta_{22} \delta V_{xc} / \delta v_0 \cdot v_2^2 \end{aligned} \quad (32)$$

Further let us give the short comment regarding constants β_{ik} . Indeed, 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 [18]. In any case it requires a careful check. Obviously, the terms with constants β_{01} , β_{11} , β_{12} , β_{22} should be neglected (at least in the zeroth approximation in comparison with others), so they can be equal to 0. 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]:

$$F_{sp} = \left\{ 1 - \frac{\partial}{\partial \epsilon} \sum_{kk} [-(V.I.P.)_k] \right\} \quad (33)$$

One can see that this definition is corresponding to the pole strength of the corresponding Green's function [2,11]. As potential V_{xc} we use the Gunnarsson-Lundqvist exchange-correlation functional [17]:

$$V_{xc}(r) = -(1/\pi)[3\pi^2 \cdot \rho(r)]^{1/3} - 0,0333 \cdot \ln[1 + 18,376 \cdot \rho^{1/3}(r)] \quad (34)$$

Using the above written formula, one can simply define the values (24), (33).

RESULTS AND CONCLUSIONS

In ref. [15] the above presented combined approach has been applied to analysis of the photoelectron spectrum for the sufficiently complicated from the theoretical point of view N_2 molecule, where the known Koopmans' theorem even fails in reproducing the sequence of the V. I. P.'s in the PE spectrum (c.f.[5–7]). It is stressing, however it has been possible to get the full sufficiently correct description of the diatomic PES already in the effective one-quasiparticle approximation [11, 13]. 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. The carbon oxide molecule, which is considered in this paper, has been naturally studied in many papers. (see [3–8]). In full analogy with the molecule of N_2 [15] 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 :

$$N_k(\epsilon) = \sum_{n=0}^{\infty} e^{-S} \frac{S^n}{n!} \delta(\epsilon - \epsilon_k + \Delta \epsilon_k + n \cdot \hbar\omega), \quad (35)$$

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

In case the frequencies change considerably, the intensity distribution of the most intensive lines can analogously be well approximated by an effective parameter S . In fig. 1 it is presented the experimental [5,6] PES for the CO molecule together with the theoretical one, calculated with g^0 and Eq. (35).

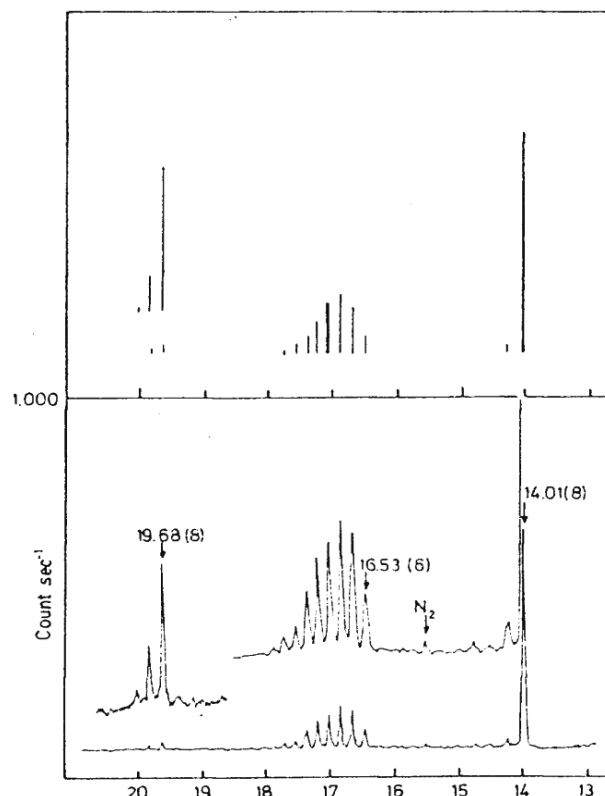


Fig. 1. Experimental and calculated (the uppermost spectrum is calculated with S^0 and Eq. (35)) photoelectron spectrum of the CO molecule (see text).

We will mean that S^0 denotes the constant S calculated with g^0 and S^{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 we listed the experimental and calculated (our data) values of S .

Table I
Experimental and calculated (our data) values of

S^0			S^{exp}		
5σ	1π	4σ	5σ	1π	4σ
0.045	2.394	0.262	0.04	2.30	0.27 ^b

One could guess that there a physically reasonable agreement between the theoretical and experimental results for all three bands. It should be noted that more sophisticated calculation by Cederbaum et al [11] 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^{exp} . This example also confirms that quite simple theory become an effective tool in interpreting the vibrational structure of the molecular PES, especially taking into account an essential simplification (implementation of the DFT scheme) of the standard Green's function approach. At last, we should note that the presented combined GF-DFT approach can be very helpful for multi-atomic molecules, especially for larger ones, when full *ab initio* calculations can be not available.

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A. P. Fedchuk, A. V. Glushkov, Ya.I. Lepikh, A. V. Loboda, Yu. M. Lopatkin, A. A. Svinarenko

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

Abstract.

The combined theoretical approach to vibrational structure in photoelectron spectra (PES) of molecules, which is based on the density functional theory (DFT) and the Green's-functions (GF) approach, is used for quantitative treating the carbon oxide molecule PES.

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

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А. В. Глушков, Я. И. Лепих, А. П. Федчук, А. В. Лобода, Ю. М. Лопаткин, А. А. Свиarenко

МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ В ОПРЕДЕЛЕНИИ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ ФОТОЭЛЕКТРОННОГО СПЕКТРА МОЛЕКУЛЫ СО

Резюме.

Комбинированный теоретический метода описания колебательной структуры для фотоэлектронных спектров молекул, который базируется на методе функций Грина и теории функционала плотности (ТФП), применен к количественному описанию фотоэлектронного спектра молекулы СО

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

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О. В. Глушков, Я. І. Леніх, О. П. Федчук, А. В. Лобода, Ю. М. Лопаткін, А. А. Свиarenко

МЕТОД ФУНКЦІЙ ГРИНА І ФУНКЦІОНАЛУ ГУСТИНИ У ВИЗНАЧЕННІ ВІБРАЦІЙНОЇ СТРУКТУРИ ФОТОЕЛЕКТРОННОГО СПЕКТРУ МОЛЕКУЛИ СО

Резюме.

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 молекули СО.

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