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THE GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRONIC SPECTRA: MOLECULES OF CH, HF

The combined theoretical approach to vibrational structure in photo-electronic spectra (PES) of molecules is used for quantitative treating of PES of the CH, HF molecules. The method is based on the density functional theory (DFT) and the Green's-functions (GF) approach.

Many papers have been devoted to the treatment of the vibrational spectra by construction of potential curves for the reference molecule (the molecule due to be ionized) and the molecular ion (c. f. [1—19]). The most sophisticated method is provided by the GF approach. Usually, the electronic GF is defined for the 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 at least a part of these data are unavailable, the calculations have been carried out with the objective of determining the missing data through comparison with experiment. To avoid this difficulty and to gain the additional information about the ionization process, L. S. Cederbaum et al [11] have extended the GF approach to include the vibration effects and shown that the GF method allows *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].

Earlier, has been developed the combined GF-DFT approach [12—15] to the vibration structure in PES of the molecules, which has been successfully applied to quantitative treatment of the CO and N_2 molecules. Here we have applied this method to the determination of the key parameters of the CH, HF molecules PES. It is important to note that the calculation procedure of the GF-DFT method is significantly simplified. As the key aspects of the GF-DFT method has been in details earlier considered, we are only limited to presentation of the main formulae.

The quantity which contains the information about the ionization potentials (IP) and molecular vibration structure due to quick ionization is the density of occupied states [2, 8]:

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

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

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

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:

$$H = T_{\mathrm{E}}(\partial/\partial x) + T_{\mathrm{N}}(\partial/\partial X) + U_{\mathrm{EE}}(x) + U_{\mathrm{NN}}(X) + U_{\mathrm{EN}}(x, X), \quad (3)$$

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 electronic or nuclear coordinates. As usually, introducing a field operator $\Psi(R,\theta,x) = \sum_i \phi_i(x,R,\theta)a_i(R,\theta)$ assuming that 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 on the HF ground state; R_0 is the equilibrium geometry on the HF level) and dimensionless normal coordinates Q_s one could write the standard Hamiltonian as follows [10, 11]:

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

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

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

$$H_{EN}^{(1)} = 2^{-1/2}\sum_{s=1}^{M}\left(\frac{\partial \mathrm{T}_i}{\partial Q_s}\right)_0 (b_s + b_s^t)[a_i^t a_i - n_i] +$$

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

$$H_{EN}^{(2)} = 2^{-3/2}\sum\sum_{s=1}^{M}\left(\frac{\partial V_{ijkl}}{\partial Q_s}\right)_0 (b_s + b_s^t)[\delta v_1 a_i^t a_j^t a_k + \\ + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t] + \\ + \frac{1}{8}\sum\sum_{s,s'=1}^{M}\left(\frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s''}}\right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t[\delta v_1 a_i^t a_j^t a_k + \\ + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t],$$

with $n_i = 1 \quad (0), \quad i \in f \quad (i \notin f), \quad \delta\sigma_f = 1 \quad (0)$, $(ijkl) \in \sigma_f$, 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_i or ϕ_l and ϕ_j are unoccupied. Here for simplicity all terms leading to non-harmonicities, are being neglected. The ω_s are the HF frequencies; b_s, b_s^t are destruction and creation operators for vibrational quanta as

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

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

$$H_0 = \sum_i \mathrm{T}_i(R_0) a_i^t a_i + \sum_{s=1}^{M}\hbar\omega_s\left(b_s^t b_s + \frac{1}{2}\right) + \\ + \sum_{s=1}^{M}\sum_i 2^{-1/2}\left(\frac{\partial \mathrm{T}_i}{\partial Q_s}\right)[a_i^t a_i - n_i](b_s + b_s^t)_0 + \\ + \sum_{s,s'=1}\sum_i \frac{1}{4}\left(\frac{\partial^2 \mathrm{T}_1}{\partial Q_s \partial Q_{s'}}\right)_0 [a_i^t a_i - n_i](b_s + b_s^t)(b_{s'} + b_{s'}^t). \tag{6}$$

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

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

$$\tilde{H}_0 = \sum_{s=1}^{M}\hbar\omega_s b_s^t b_s + \sum_{s=1}^{M} g_s^k(b_s + b_s^t) + \\ + \sum_{s,s'=1}^{M}\gamma_{ss'}^k(b_s + b_s^t)(b_{s'} + b_{s'}^t), \tag{8}$$

$$g_s^i = \pm\frac{1}{\sqrt{2}}\left(\frac{\partial \mathrm{T}_i}{\partial Q_s}\right)_0, \quad \gamma_{ss'}^i = \pm\frac{1}{4}\left(\frac{\partial^2 \mathrm{T}_i}{\partial Q_s \partial Q_{s'}}\right)_0. \tag{9}$$

Introducing new operators

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

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

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

Eq. (7) is as follows:

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

where δ function in (12) naturally contains the information about adiabatic ionization potential and the spacing of the vibration peaks; while $|\langle\hat{n}|U|0\rangle|^2$ 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 [3, 10, 11]:

$$G_{kk'}(\mathrm{T}) = -i\hbar^{-1}\int_{-\infty}^{\infty}\mathrm{d}t e^{i\hbar^{-1}\epsilon t}\langle\psi_0|''\{a_k(t)a_k^t(0)\}|\psi_0\rangle \tag{13}$$

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

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

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

$$G_{kk'}^{\mathrm{OB}}(t) = \pm\delta_{kk'} i\exp[-in^{-1}(\varepsilon_k \mp \Delta\varepsilon)t]\times \\ \times\sum_n|\langle\hat{n}_k|U_k|0\rangle|^2\exp(\pm in_k\cdot\hat{\omega}_k t). \tag{15}$$

The corresponding Dyson-like equation ($\Sigma = O$) looks as follows:

$$G_{kk'}(\in) = G_{kk'}^{\mathrm{OB}}(\in) + \sum_{kk'} G_{kk}^{\mathrm{OB}}(\in)\Phi_{kk''}G_{k''k'}(\in), \tag{16}$$

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

where $U_{n_i i} = |\langle\hat{n}_i|U_i|0\rangle|^2$ and

$$E_i = \in_i \mp \Delta\in_i \mp \hat{n}_i\cdot\hat{\omega}_i. \tag{17}$$

The direct method for calculation of $N_k(\in)$ as the imaginary part of the GF includes a definition of the vertical IP (VIP) of the reference molecule and then of $N_k(\in)$. The zeros of the functions

$$D_k(\in) = \in - [\in^{\mathrm{op}} + \Sigma(\in)]_k, \tag{18}$$

where $(\in^{\mathrm{op}} + \Sigma)_k$ denotes the k-th eigen-value of the diagonal matrix of the one-particle energies added to matrix of the self-energy part, are the negative VIP for a given geometry. One could write according to [10, 11]:

$$(\mathrm{V.I.P.})_k = -(\in_k + F_k), \\ F_k = \Sigma_{kk}(-(\mathrm{V.I.P.})_k) \approx \frac{1}{1 - \partial\Sigma_{kk}(\in_k)/\partial_\in}\Sigma_{kk}(\in_k). \tag{19}$$

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 δQ_S, and new coupling constants are then:

$$g_l = \pm(1/\sqrt{2})[\partial(\in_k + F_k)/\partial Q_l]_0,$$
$$\gamma_{ll'} = \pm\left(\frac{1}{4}\right)[\partial^2(\in_k + F_k)/\partial Q_l/\partial Q_{l'}]_0. \quad (20)$$

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:

$$\sum{}_{kk}^{(2)}(\in) = \sum_{\substack{i,j \\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} \quad (21)$$

and the coupling constant g_l, could be written as

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

$$q_k = \frac{\sum \frac{(V_{ksij} - V_{ksji})^2}{[-(\text{V.I.P.})_k + \in_s - \in_i - \in_j]^2}\left[\frac{\partial \in_s}{\partial Q_l} - \frac{\partial \in_i}{\partial Q_l} - \frac{\partial \in_j}{\partial Q_l}\right]}{\frac{\partial \in_k}{\partial Q_l}\sum \frac{(V_{ksij} - V_{ksji})^2}{[-(\text{V.I.P.})_k + \in_s - \in_i - \in_j]^2}}. \quad (23)$$

It is suitable to use the pole strength of the corresponding GF in the form of [12]:

$$\rho_k = \left\{1 - \frac{\partial}{\partial\in}\sum{}_{kk}[-(\text{V.I.P.})_k]\right\}^{-1};\ 1 \geqslant \rho_k \geqslant 0, \quad (24)$$

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

Below we give the DFT definition of the pole strength corresponding to VIP and confirm the earlier data [10, 11]: as $p_k \approx 0{,}8$—$0{,}95$. 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 quasi-particle Fermi-liquid version of the DFT, following to Refs. [12, 13, 19]. The master equation could be derived using an expansion for self-energy part Σ into set on degrees of x, ε-ε_F, p^2-p_F^2 (here ε_F and p_F are the Fermi energy and pulse correspondingly):

$$[p^2/2 - \sum_\alpha Z_\alpha/r_\alpha + \sum{}_0(x) + p(\partial\sum/\partial p^2)p]\Phi_\lambda(x) =$$
$$= (1 - \partial\sum/\partial\varepsilon)\varepsilon_\lambda\Phi_\lambda(x). \quad (27)$$

The functions Φ_λ in (27) are orthogonal with a weight $\rho_k^{-1} = a^{-1} = [1 - \partial\sum/\partial\varepsilon]$. Now one can introduce the wave functions of the quasi-particles $\varphi_\lambda = a^{-1/2}\Phi_\lambda$, which are, as usually, orthogonal with weight 1. The equations (27) could 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 quasi-particle densities:

$$\nu_0(r) = \sum_\lambda n_\lambda |\Phi_\lambda(r)|^2,$$
$$\nu_1(r) = \sum_\lambda n_\lambda |\nabla\Phi_\lambda(r)|^2,$$
$$\nu_2(r) = \sum_\lambda n_\lambda[\Phi_\lambda^*\Phi_\lambda - \Phi_\lambda^*\Phi_\lambda].$$

The densities ν_0 and ν_1 are similar to the HF electron density and kinetic energy density correspondingly; the density ν_2 has no analogs in the HF or DFT theory and appear as a result of the account for the energy dependence of the mass operator Σ. A Lagrangian L_q could be written as a sum of a free Lagrangian and Lagrangian of interaction: $L_q = L_q^0 + L_q^{\text{int}}$, where a free Lagrangian L_q^0 has a standard form:

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

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:

$$L_q^{\text{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2}\int\beta_{ik}F(r_1, r_2)\nu_i(r_1)\nu_k(r_2)dr_1dr_2, \quad (29)$$

where β_{ik} are some constants (please, look below), F is an effective potential of the exchange-correlation interaction. The Coulomb interaction part L_K looks as follows [19]:

$$L_K = -\frac{1}{2}\int[1 - \sum{}_2(r_1)]\nu_0(r_1)[1 - \sum{}_2(r_2)] \times$$
$$\times\nu_0(r_2)/|r_1 - r_2|dr_1dr_2, \quad (30)$$

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

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

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

$$\Sigma_0 = (1 - \Sigma_2)V_K + \Sigma_0^{\text{ex}} + \frac{1}{2}\beta_{00}\delta^2V_{\text{XC}}/\delta\nu^2\nu_0^2 +$$
$$+ \beta_{00}\delta V_{\text{XC}}/\delta\nu_0\nu_0 + \beta_{01}\delta V_{\text{XC}}/\delta\nu_0\nu_1 +$$
$$+ \beta_{01}\delta^2V_{\text{XC}}/\delta\nu_0^2 \cdot \nu_0\nu_1 + \beta_{02}\delta^2V_{\text{XC}}/\delta\nu_0^2 \cdot \nu_0\nu_2 +$$
$$+ \beta_{02}\delta V_{\text{XC}}/\delta\nu_0 \cdot \nu_2. \quad (31)$$

$$\Sigma_2 = \beta_{02}\delta V_{\text{XC}}/\delta\nu_0 \cdot \nu_0 + \beta_{12}\delta V_{\text{XC}}/\delta\nu_0 \cdot \nu_1 +$$
$$+ \beta_{22}\delta V_{\text{XC}}/\delta\nu_0 \cdot \nu_2. \quad (32)$$

Here V_K is the Coulomb term, Σ_0^{ex} is the exchange term. Using the known canonical relationship, one can derive the quasi-particle Hamiltonian [10, 14], corresponding to L_q.

In refs. [12, 13, 15] it has been given the comment regarding the 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-system theory. The value of β_{00} depends on the definition of V_{xc}. If for V_{xc} one of the DFT exchange-correlation potentials form is used, then, without losing a generality of the statement, $\beta_{00} = 1$. The constant β_{02} can be in principle calculated by the analytical way, but it is very useful to remember its connection with a spectroscopic factor F_{sp} of the system [19]:

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

One could 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]:

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

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

In refs. [15, 20], 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 and CO molecules, 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 that it has been possible to get the full sufficiently correct description of the diatomics PES already in the effective one-quasiparticle approximation [11, 13]. Another essential aspect is the sufficiently simple calculating procedure, provided by using the DFT. Moreover, the cumbersome calculation is not necessary here, if the detailed Hartree—Fock (Hartree—Fock—Rothaan) 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 could be well approximated using only one parameter g:

$$N_k(\epsilon) = \sum_{n=0}^{\infty} e^{-s} \frac{S^n}{n!} \delta(\epsilon - \epsilon_k + \Delta\epsilon_k + n \cdot \hbar\hat{\omega}), \\ S = g^2(\hbar\omega)^{-2}. \qquad (35)$$

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 table 1 the experimental (S^{exp}) and theoretical (S^{th}) values of the S parameter are presented for the molecules of CH and HF: S^0 is the value without accounting correlation and reorganization corrections; $S^{(b)}$ — the values of the parameter with accounting of the correlation and reorganization, in total synergistic, corrections within our combined GF—DFT method.

Table 1

The experimental (S^{exp}) and theoretical (S^{theor}) values of the S parameter 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	Theory	S^{theor}		S^{exp}	
		1	2	1	2
CH	S^0	0.22(1π)	0.105(3σ)	—	—
	$S^{(b)}$	0.2711	0.1134		
HF	S^0	0.126(1π)	1.90(3σ)	0.35	2.13
	$S^{(b)}$	0.1920	2.0534		

One could guess that there a physically reasonable agreement between the theoretical and experimental results for all bands. This example also confirms that quite effective 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 GF approach.

In conclusion let us indicate on the prospects of the presented method application to the problems of the cooperative laser-electron-vibrational gamma-nuclear effects in the di-atomics and multi-atomic molecules [21].

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THE GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRONIC SPECTRA: MOLECULES CH AND HF

Abstract
The improved theoretical approach to vibration structure of photo-electronic spectra (PES) of molecules is used for quantitative treatment of the CH, HF molecules PES. The method is based on the density functional theory (DFT) and the Green's-functions (GF) approach including synergistic corrections.
Key words: photo-electronic spectra, Green's functions, density functional theory, CH and HF molecules, synergistic corrections.

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МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ В ОПРЕДЕЛЕНИИ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ ФОТОЭЛЕКТРОННОГО СПЕКТРА: МОЛЕКУЛЫ CH, HF

Резюме
Улучшенный теоретический метод описания колебательной структуры фотоэлектронных спектров молекул, который базируется на методе функций Грина и теории функционала плотности (ТФП), включая синергетические поправки, применен к количественному описанию фотоэлектронных спектров молекул CH, HF.
Ключевые слова: фотоэлектронный спектр, метод функций Грина, теория функционала плотности, молекулы CH и HF, синергетические поправки.

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МЕТОД ФУНКЦІЙ ГРІНА І ФУНКЦІОНАЛУ ГУСТИНИ У ВИЗНАЧЕННІ ВІБРАЦІЙНОЇ СТРУКТУРИ ФОТОЕЛЕКТРОННОГО СПЕКТРУ: МОЛЕКУЛИ CH, HF

Резюме
Покращений теоретичний метод опису вібраційної структури фотоелектронних спектрів молекул, який базується на методі функцій Гріна та теорії функціоналу густини, включаючи синергетичні поправки, застосовано до кількісного опису фотоелектронних спектрів молекул CH, HF.
Ключові слова: фотоелектронний спектр, метод функцій Гріна, теорія функціоналу густини, молекули CH та HF, синергетичні поправки.