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THE GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRON SPECTRA OF MOLECULES: REVIEW OF METHOD

We present the basis's of the new combined theoretical approach to vibrational structure in photoelectron spectra of molecules. The approach is based on the Green's function method, which generalizes the Cederbaum-Domske formalism, and quasiparticle density functional theory. It generalizes the known Green's function approach by It is presented a new procedure for determination of the density of states, which describe the vibrational structure in molecular photoelectron spectra

I. Introduction

A number of phenomena, provided by interaction of electrons with vibrations of the atomic nuclei in molecules or solids under availability of of the electron states degeneration is usually called as the Jahn-Teller effect. This interaction may lead to local deformations, which are the reason of the structural phase transitions in the solids (statical Jahn-Teller effect)or appearance of the connected electron-vibrational states (a dynamical Jahn-Teller effect) [1-4]. Indeed, the physics of the interaction of electrons with vibrations of the atomic nuclei in molecules or solids is more richer (c.f.[1-111]). One could mention here a great field of the resonant collisions of electrons with molecules, which are one of the most efficient pathways for the transfer of energy from electronic to nuclear motion. While the corresponding theory has been refined over the years with sophisticated and elaborate non-local treatments of the reaction dynamics, such studies have for the most part treated the nuclear dynamics in one dimension. This situation has resulted from the fact that, as the field of electron-molecule scattering developed, both experimentally and theoretically, the phenomena of vibrational excitation and dissociative attachment were first understood for diatomics, and it seemed natural to extend that understanding to polyatomic molecules using 1-D or single-mode models of nuclear motion. However a series of experimental measurements of these phenomena in small polyatomic molecules have proven to be uninterpretable in terms of atomic motion with single degree of freedom. Reader can find more details about this topic in the recent paper by Rescigno et al [4].

In last several decades quantum chemistry methods has been refined with a sophisticated and comprehensive approaches of the correct interelectron correlations and electron-nuclear dynamics treatments [9-49]. Very interesting quote has been indicated by Bartlett and Musiał and earlier by Wilson: "*Ab initio quantum chemistry is an emerging computational area that is fifty years ahead of lattice gauge theory and a rich source of new ideas and new approaches to the computation of many fermion systems"* [26]. Following to ref. [26] we repeat that *d*riving these developments are the types of problems addressed by quantum chemists, as shown in Fig. 1. Primary among these are potential-energy surfaces (PES) which describe the behavior of the electronic energy with respect to the locations of the nuclei, subject to the underlying Born-Oppenheimer or clamped nuclei approximation. From the ground- and excited-state wave functions one could in principle obtain all properties that arise from a solution to vibrational Schrödinger equation that gives the frequencies and with derivatives of the dipole moment, the infrared intensities [26-39]. Electronic excited states are also accessible along with electronic and photo-electron spectra. The properties that arise from the one-particle density matrix, such as dipole moments, hyperfine coupling constants, and electric-field gradients, are readily available.

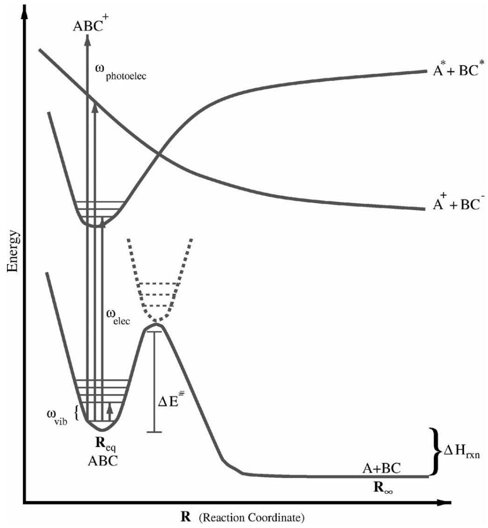

Figure 1. The nature of quantum chemical problems (from ref. [26]).

From even higher-order electric-field derivatives, one obtains hyperpolarizabilities, which determine nonlinear optical behavior. From derivatives relative to atomic displacements in molecules, one obtains anharmonic effects on vibrational-rotational spectra. In result , one could mention that a main objective is an accurate solution of the Schrödinger equation for molecules composed of comparatively light elements.

As it is often takes a place, the old multi-body quantum theoretical approaches, which have been primarily developed in a theory of superfluity and superconductivity, and generally speaking in a theory of solids, became by the powerful tools for developing new conceptions in molecular calculations [50-65]. Many of them offers a synthesis of cluster expansions, Brueckner's summation of ladder diagrams, the summation of ring diagrams Gell-Mann and an infinite-order generalization of many-body perturbation theory MBPT (Kelly, 1969; Bartlett and Silver, 1974a, 1976. Using quantum-field methods in molecular theory allowed to obtain a very powerful approach for correlation in many-electron systems. Only with this property are applications to polymers, solids, or the electron gas possible, and, even for small molecules, its effects are numerically quite significant. Configuration interaction methods, long the focus of the correlation problem in quantum chemistry Shavitt, 1998, do not, in general, have this property which is responsible for the emphasis on the coupled cluster theory and its multi-body perturbation theory approximations (Kelly, 1969; Bartlett and Silver, 1974a, 1974b; Pople *et al.*, 1976) in chemistry. For more details, the history of coupled cluster theory is best told from the viewpoint of some of its principal developers (look review [26]).

The Green's method is very well known in a quantum theory of field, quantum electrodynamics , quantum theory of solids (c.f.[61-63]). Naturally, an attractive idea was to use it in the molecular calculations. Returning to problem of description of the vibrational structure in photoelectron spectra of molecules, it is easily understand that this approach has great perspective as it was shown by Cederbaum et al (c.f.[65-68]). One could note that the experimental photoelectron (PE) spectra usually show a pronounced vibrational structure. 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 Green's function is defined for fixed position of the nuclei. As result, only vertical ionization potentials (V.I.P.'s) can be calculated [65]. 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. One could agree here that highly accurate calculations are necessary to obtain good results with the above methods. To avoid this difficulty and to gain additional information about the ionization process, Cederbaum et al [65-

68] extended the Green's functions approach to include the vibrational effects and showed that the Green's functions method allowed the *ab initio* calculation of the intensity distribution of the vibrational lines, of the vibrational frequencies of the reference molecule and its ions, and of geometry shifts due to ionization and particle attachment. Besides, a great advancement here is connected with a possibility of the quite exact calculation of ionization potentials (I.P.'s) for molecules. According to ref.[65], starting from Hartree-Fock (HF) calculation [71,72] the electronic Green's functions have been calculated applying a many-body perturbation expansion. In this method the Koopmans' defect, i.e., the difference between the I.P. and the value derived from the Koopmans' theorem, is calculated directly, avoiding the usual subtraction of large numbers of roughly equal magnitude.

Further let us remember that for larger molecules and solids, far more approximate but more easily applied methods such as density-functional theory (DFT) [40-42] or from the wave-function world the simplest correlated model MBPT are preferred. Indeed, in the last decades DFT theory became by a great, quickly developing field of the modern quantum computational chemistry of atoms, molecules, solids. Naturally, this approach does not allow to reach a spectroscopic accuracy in description of the different molecular properties, nevertheless, the key idea is very attractive and can be used in new combined theoretical approaches.

Here we present the basis's of the new combined theoretical approach to vibrational structure in photoelectron spectra of molecules. The approach is based on the Green's function method and Fermi-liquid DFT formalism [80-86]. It generalizes the known Green's function approach by Cederbaum-Domcke (we use this version as a starting basis). 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. In all cases no data about the molecular ion are needed and all transitions except those between linear and bent configurations are included. 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 calculation becomes a powerful tool in interpreting the vibrational structure of photoelectron spectra for different molecular systems.

2. The combined Green's functions and density functional approach

2.1 The Hamiltonian of the system. The density of states in one –body solution

According to [65], the quantity which contains the information about the ionization potentials and the molecular vibrational structure due to quick ionization is the density of occupied states[9]:

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

where $|\Psi_0\rangle$ is the exact ground state wavefunction 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:

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

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 corresponding Hamiltonian is as follows:

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

where T_{E} is the kinetic energy operator for the electrons, T_{N} is the kinetic energy operator for the nuclei, and U represents the interaction

$$U(x,X) = U_{\mathrm{EE}}(x) + U_{\mathrm{N\,N}}(X) + U_{\mathrm{EN}}(x,X), \quad (4)$$

where x denotes electron coordinates, X denotes nuclear coordinates, $U_{\mathbb{E}}$ represents the Coulomb interaction between electrons, etc.Below we follow to original version of the Cederbaum-Domske approach to vibrational structure of the molecular spectra. Further the following field operator is usually introduced:

$$\Psi(R,\theta,x) = \sum_i \phi_i(x,R,\theta)a_i(R,\theta) \qquad (5)$$

where the ϕ_i are Hartre-Forck (HF) one–particle functions and the a_i are destruction operators for a HF particle in the state described by the subscript *i*. Fixing $\theta(\theta = \theta_0)$, the Hamiltonian in the occupation number representation is given by [65]

$$H = H_{\mathrm{EN}}(R,\theta_0) + U_{\mathrm{N\,N}}(R,\theta_0) + T_{\mathrm{N}}(\partial/\partial R), \qquad (6)$$

$$H_{EN} = \sum_i \epsilon_i(R)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R)a_i^t a_j^t a_l a_k$$

$$-\sum_{ij}\sum_{k\in f}[V_{ikkj}(R)]a_i^t a_j, \qquad (7)$$

$$V_{ijkl} = \langle ij|e^2|r-r'|^{-1}|kl\rangle$$

The $\in_i(R)$ are the one-particle HF energies and f denotes the set of orbitals occupied in the HF ground state. As usually in the adiabatic approximation one could write the eigenfunctions to H as products $|x,R,\theta_0\rangle_E \times |R\rangle_N$,and further expand $\in_i(R)$, $V_{ijkl}(R)$, and $U_N\ (R,\theta)$ about R_0 leaving the operators a_i and a_i^t unchanged:

$$H = \sum_i {}^o{}_i(R_0)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R_0)a_i^t a_j^t a_l a_k -$$

$$-\sum_j\sum_{k\in f}[V_{ikjk}(R_0) - V_{ikkj}(R_0)]\,a_i^t a_j + +\sum_i\Big[\sum_{s=1}^{M}\left(\frac{\partial \in_1}{\partial R_s}\right)_0 (R - R_{s0}) +$$

$$+\frac{1}{2}\sum_i\sum_{s,s'=1}^{M}\left(\frac{\partial^2 \in_i}{\partial R_s \partial R_{s'}}\right)_0 (R_s - R_{s0})(R_{s'} - R_{s'0})\Big]a_i^t a_i + \ldots + U_N\ (R_0,\theta_0) + \ldots + T_N\left(\frac{\partial}{\partial R}\right)$$

(8)

where M is the number of normal coordinates.

Choosing R_0 as the equilibrium geometry on the HF level and introducing dimensionless normal coordinates Q_s one can write the following Hamiltonian (the subscript 0 stands for R_0):

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

$$H_E = \sum_i \epsilon_i(R_0)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R_0)a_i^t a_j^t a_l a_k -$$

$$-\sum_{i,j}\sum_{k\in f}[V_{ikjk}(R_0) - V_{ikkj}(R_0)]a_i^t a_j \quad ,$$

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

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

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

$$H_{EN}^{(2)} = 2^{-3/2}\sum\sum_{s=1}^{M}\left(\frac{\partial V_{ijkl}}{\partial Q_s}\right)_0 (b_s + b_s^t)[\delta v_1\, a_i^t a_j^t a_k + \qquad (9)$$

$$+\delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t]$$

$$\frac{1}{8}\sum\sum_{s,s'=1}^{M}\left(\frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s''}}\right)_0 (b_s + b_s^t)(b_{s'} +$$

$$+b_{s'}^t[\delta v_1\, a_i^t a_j^t a_k + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t]$$

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. Besides, here for simplicity all terms leading to anharmonicities are neglected. The ω_s are the HF frequencies and the b_s and b_s^t are destruction and creation operators for vibrational quanta defined by

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

$$\partial/\partial Q_s = (1/\sqrt{2})(b_s - b_s^t) \qquad (10)$$

The interpretation of the above Hamiltonian is given in ref. [3]. The first term H_E describes the electronic motion for nuclei fixed at the HF ground state geometry. The second term H_N describes the motion of the nuclei in the harmonic HF potential (the extension to anharmonic terms can easily be done). $H_{EN}^{(1)}$ represents the coupling of the HF particles with the nuclear motion. The coupling constants are the normal coordinate derivatives of the HF one-particle energies. The first sum in the expression for $H_{EN}^{(1)}$ is responsible for the geometry shifts and the second one for the charge of frequencies due to electronions. There is also a modification of the interaction between electrons through the coupling to the nuclear motion. The term $H_{EN}^{(2)}$, which describes this modification, is due to its nature less important than $H_{EN}^{(1)}$. The exact solution of the one-body HF problem has been given in ref.[65] too. The HF-single-particle component H_0 of the Hamiltonian (9) is as follows:

$$H_0 = \sum_i \epsilon_i(R_0)a_i^t a_i + \sum_{s=1}^{M} \hbar\omega_s(b_s^t b_s + \frac{1}{2}) + \\ + \sum_{s=1}^{M} \sum_i 2^{-1/2}\left(\frac{\partial \epsilon_i}{\partial Q_s}\right)[a_i^t a_i - n_i](b_s + b_s^t)_0 + \\ + \sum_{s,s'=1} \sum_i \frac{1}{4}\left(\frac{\partial^2 \epsilon_1}{\partial Q_s \partial Q_{s'}}\right)_0 [a_i^t a_i - n_i](b_s + b_s^t)(b_{s'} + b_{s'}^t) \tag{11}$$

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

$$N_k^0({}^o) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dte^{i\hbar^{-1}q} \langle\Phi_0|\ a_k^t(0)a_k(t)|\ \Phi_0\rangle, \quad k \in f, \tag{12}$$

and the density of unoccupied states by

$$N_k^0({}^o) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dte^{i\hbar^{-1}q} \langle\Phi_0|\ a_k(t)a_k^t(0)|\ \Phi_0\rangle, \\ k \notin f \tag{13}$$

with $$a_k(t) = e^{i\hbar^{-1}H_{0^t}} a_k e^{-i\hbar^{-1}H_0 t}. \tag{14}$$

Here $|\Phi_0\rangle$ is the product of the electronic and vibrational ground states, i.e., $|\Phi_0\rangle = |\ \Phi_0\rangle|\ 0\rangle$, where $|\Phi_0\rangle$ is the ground state to the HF operator $\sum {}^o{}_i(R_0)a_i^t a_i$ and $|\ 0\rangle$ is the state containing no vibrational quantum, i.e., $b_s|\ 0\rangle = 0$ for all s. From Definitions (12) and (13) it follows immediately that

$$N_k^0({}^o) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dte^{i\hbar^{-1}({}^o - {}^o{}_k)t}\langle 0|\ e^{\pm i\hbar^{-1}\widetilde{H}_{0^t}}|0\rangle, \tag{15}$$

with

$$\widetilde{H}_0 = \sum_{s=1}^{M} \hbar\omega_s b_s^t b_s + \sum_{s=1}^{M} g_s^k(b_s + b_s^t) \\ + \sum_{s,s'=1}^{M} \gamma_{s'}^k(b_s + b_s^t)(b_{s'} + b_{s'}^t) \tag{16}$$

where

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

(17), (18)

As a first step in the evaluation of Eg. (15) new operators

$$c_s = \sum_{l=1}^{M} (\lambda_1^{sl} b_l + \lambda_2^{sl} b_l^t) \tag{19}$$

with real coefficients λ_1^{sl}, λ_2^{sl} were introduced in ref. [65]. The coefficients λ_1^{sl}, λ_2^{sl} are now determined in such a way that $\widetilde{H}_0$, expressed in the new operators, takes the form

$$\widetilde{H}_0 = \sum_{s=1}^{M} \hbar\hat{\omega}_s c_s^t c_s + \sum_{s=1}^{M} \hat{g}_s(c_s + c_s^t) + k. \tag{20}$$

Inserting the inverse transformation

$$b_s = \sum_{l=1}^{M} \lambda_1^{ls} c_l - \lambda_2^{ls} c_l^t) \tag{21}$$

in Eg. (16) and comparing with Eg. (21) we obtain the equations

$$\sum_l \hbar\omega_l(\lambda_1^{sl}\lambda_1^{s'l} + \lambda_2^{sl}\lambda_2^{s'l}) + \\ 2\sum_{ll'} \gamma_{ll'}(\lambda_1^{sl} - \lambda_2^{sl})(\lambda_1^{s'l'} - \lambda_2^{s'l'}) = 0 \quad (s \neq s') \tag{22}$$

$$\sum_{l} \hbar\omega_l(\lambda_1^{s'l}\lambda_2^{sl} + \lambda_1^{sl}\lambda_2^{s'l}) -$$

$$-2\sum_{ll'} \gamma_{l'}(\lambda_1^{sl} - \lambda_2^{sl})(\lambda_1^{s'l'} - \lambda_2^{s'l'}) = 0 \qquad (23)$$

$$\hbar\hat{\omega}_s = \sum_{l} \hbar\omega_l(\lambda_1^{sl} + \lambda_2^{sl})^2, \qquad (24)$$

$$\hat{g}_s = \sum_{l} g_l(\lambda_1^{sl} + \lambda_2^{sl}) , \qquad (25)$$

$$k = \sum_{l} \frac{1}{2}(\hbar\hat{\omega}_l - \hbar\omega_l). \qquad (26)$$

Equation (22) and (23) together with Egs. (18) and (19) constitute a system of $2M^2$ independent equations for the $2M^2$ unknown coefficients λ_1^{sl}, λ_2^{sl}. Solution of this system yields the change in normal coordinates in terms of the coupling constants $\gamma_{s'}$.. Equations (24)-(26) determine the vibrational frequencies $\hat{\omega}_s$ of tion, the new coupling parameters $\hat{g}_s$ and the constant k.

The nexy unitary operator $U = \prod_{l=1}^{M} \exp[f_l(c_l - c_l^t)]$ diagonalizes $\widetilde{H}_0$ if $f_l = \hat{g}_l / \hbar\hat{\omega}$ is chosen:

$$U\widetilde{H}_0U^t = \sum_{s} \hbar\hat{\omega}_s c_s^t c_s + \Delta^o \qquad (28)$$

with $\Delta^o = k - \sum_{s} \hat{g}_s^2 / \hbar\hat{\omega}_s$. Then the equation (14) can be rewritten as follows [13]:

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar}\int dt \exp[i\hbar^{-1}(\epsilon - \epsilon_k \pm \Delta\epsilon_k)t]$$
$$\langle 0|\, U^t \exp\left(\pm i\sum_{s}\hat{\omega}_s c_s^t c_s t\right)U|\, 0\rangle \qquad (30)$$

or using the symbol $|\,\hat{n}\rangle$ for states belonging to operators c_s, i.e., $c_s^t c_s|\,\hat{n}\rangle = n_s|\,\hat{n}\rangle$, the density of states takes the form

$$N_k^0(^o) = \sum_{n_1\cdots n_M} |\,\langle\hat{n}\,|U\,|0\rangle\,|^2 \delta(^o - {^o}_k \pm \Delta^o{}_k \pm n\cdot\hbar\hat{\omega}) \qquad (31)$$

Further naturally the δ function in Eg. (31) contains the information about the adiabatic ionization potential and the spacing of the vibrational peaks, whereas the squared matrix element $|\,\langle\hat{n}\,|U\,|0\rangle\,|^2$ is the well-known Franck-Condon factor, which gives the intensity distribution of the vibrational spectrum. Following to ref. [65] one can decompose the matrix element $\langle\hat{n}\,|U\,|0\rangle$ as

$$\langle\hat{n}\,|U\,|0\rangle = \sum_{m_1\cdots m_M} \langle\hat{n}|\,U|\,\hat{m}\rangle\langle\hat{m}|\,0\rangle. \qquad (32)$$

where $\langle\hat{m}|\,0\rangle$ is the overlap of unshifted wave functions of different frequency and $\langle\hat{n}|\,U|\,\hat{m}\rangle$ is the overlap integral between shifted oscillator wave functions of the same frequency, which is calculated:

$$\langle\hat{n}|\,U|\,\hat{m}\rangle = \prod_{l=1}^{M} e^{-(1/2)f_l^2}\left(\frac{m_l!}{n_l!}\right)^{1/2}(-f_l)^{n_l-m_l}L_{m_l}^{n_l-m_l}(f_l^2) \qquad (33)$$

Here L_m^k is the generalized Laguerre polynomial and $f_l = \hat{g}_l / \hbar\hat{\omega}_l$. A procedure for calculating the overlap integrals $\langle\hat{m}|\,0\rangle$ wis described in ref. [65]. In order to reveal explicitly the connection between the quantities $f_l, \lambda_1^{sl}, \lambda_2^{sl}$ and the geometry shifts and frequency changes it is written as

$$\bar{\hat{Q}} = JQ + \hat{K}', \qquad (35)$$

where the vector Q denotes the normal coordinates in the ground state of the reference molecule and $\hat{Q}$ denotes the normal coordinates of the ion, both on the one-particle level. If L and $\hat{\mathrm{L}}$ are the transformation matrices from internal to normal coordinates in the initial and final states, respectively, R is the change in equilibrium position and Γ, $\tilde{\hat{\mathrm{A}}}$are the diagonal matrices of frequencies $\omega_s/\hbar$, $\hat{\omega}_s/\hbar$, then

$$\mathrm{J} = \hat{\Gamma}^{1/2}\hat{\mathrm{L}}^{-1}\mathrm{L}\Gamma^{-1/2},$$
$$\hat{\mathrm{K}} = \hat{\Gamma}^{1/2}\hat{\mathrm{L}}^{-1}\mathrm{R}\,. \qquad (36)$$

The connection between transformation matrix J, λ's is given by $\lambda_1^{s} + \lambda_2^{s} = J_{s}$, $\lambda_1^{s} - \lambda_2^{s} = J_{s}^{-1}$; normal coordinate shift $\hat{\mathrm{K}}$ is related to f_l by $f_l = \mp 2^{-1/2}\hat{K}_l$. The simplification of method is possible in case of diagonality of matrix $\gamma_{ss'}$ of coupling constants.

2.2 The Cederbaum-Domske approach to the many-body problem

Below we give the Cederbaum-Domske perturbation theory approach to *ab initio* calculation of frequencies, geometry shifts, and Franck-Condon factors starting from the one-particle picture discussed above. In a diagrammatic method in order to obtain the function $N_k(^o)$ one should calculate the Green's function $G_{\boldsymbol{k}'}(^o)$ first:

$$G_{kk'}(\epsilon) = -i\hbar^{-1}\int_{-\infty}^{\infty} dte^{i\hbar^{-1}\epsilon t}\,\langle\psi_0|\; T\{\; a_k(t)a_k^t(0)\;\}\;|\psi_0\rangle \qquad (41)$$

where *T* is Wick's time ordering operator and the function $N_k(^o)$ then follows from relation

$$\pi N_k(\epsilon) = a\,\mathrm{Im}G_{kk}(\epsilon - ai\eta)\,, \qquad (42)$$

$a = -sign^o{}_k$, where η is a positive infinitesimal. Choosing the unperturbed Hamiltonian H_0 to be

$$H_0 = \sum {}^o{}_i a_i^t a_i + H_N \qquad (43)$$

one finds for the corresponding Green's functions

$$G_{kk}^0(\epsilon) = \delta_{kk'}/(\epsilon - \epsilon_k - ai\eta) \qquad (44)$$

The Dyson equation

$$G_{kk'} = G_{kk'}^0 + \sum_{k''} G_{kk}^0\Sigma_{kk''}G_{k''k'} \qquad (45)$$

relates the Green's functions to the free ones introducing a new function $\Sigma_{kk''}(^o)$ called the (proper) self-energy part. In in order to calculate $\Sigma_{kk'}$, a well-known diagrammatic method is used. It is useful to remind that the sum of Feynman diagrams leading to the self-energy part is shown in Fig. 1. All notations are standard.

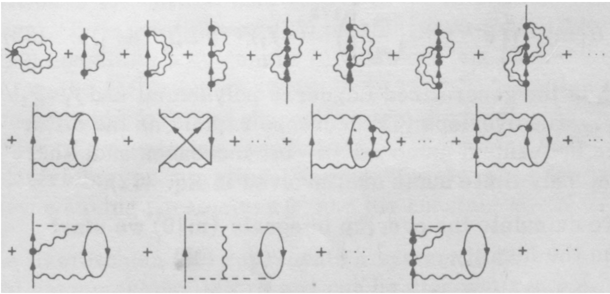

Fig. 1. The sum of diagrams contributing to the self-energy part.

The one-body problem treated above results in the exact solution of the Dyson equation with the self-energy part given by the infinite number of diagrams shown in the first row of Fig. 1 and the corresponding Green's function is as follows [65]:

$$G_{kk'}^{OB}(t) = \pm\delta_{kk'}i\exp\left[-in^{-1}(\varepsilon_k \mp \Delta\varepsilon)t\right]\times\sum_n\left|\langle\hat{n}_k|U_k|0\rangle\right|^2\exp(\pm in_k\cdot\hat{\omega}_k t) \qquad (47)$$

The corresponding Dyson-like equation is as follows:

$$G_{kk'}(\in) = G_{kk'}^{OB}(\in) + \sum_{kk'} G_{kk}^{OB}(\in)\hat{O}_{kk''}G_{k''k'}(\in) \qquad (48)$$

where $\hat{O}_{kk'}$, is equal to $\Sigma_{kk'}$, less the diagrams of the first row in Fig.1. The perturbation expansion of Φ is shown in Fig. 2 where $iG_{kk'}^{0}$, is symbolized by a double solid line.

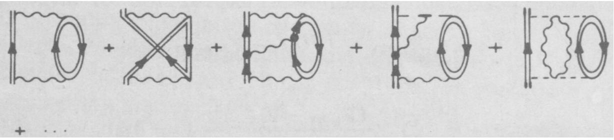

Fig. 2. Perturbation expansion of Φ_{kk}.

The expression for the sum of the first two diagrams appearing in Fig. 2 are written by a standard way:

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

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

$$U_{n_i i=}\left|\langle \hat{n}_i | U_i | 0\rangle\right|^2 \text{ and } E_i = \in_i \mp \Delta \in_i \mp h\hat{n}_i \cdot \hat{\omega}_i \quad (49)$$

The direct method for calculation of $N_k(\in)$ as the imaginary part of the corresponding Green's function implicitly includes the determination of the V. I. P. s of the reference molecule and then of $N_k(\in)$. The zeros of the functions

$$D_k(\in) = \in - \left[\in^{op} + \Sigma(\in)\right]_k, \quad (50)$$

where $(\in^{op} + \Sigma)_k$ denotes the kth eigenvalue of the diagonal matrix of the one-particle energies added to the matrix of the self-energy part, are the negative V. I. P. 's for a given geometry. Further it is easily to write:

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

$$F_k = \Sigma_{\boldsymbol{k}}\left(-(V.I.P.)_k\right) \approx \frac{1}{1 - \partial\Sigma_{\boldsymbol{k}}(\in_k)/\partial_\in}\Sigma_{\boldsymbol{k}}(\in_k). \quad (51)$$

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:

$$E_k^{N-1} = E_k^{N-1}(0) - \sum_{s=1}^{M}\left(\frac{\partial(\in_k + F_k)}{\partial Q_s}\right)_0 Q_s -$$

$$- \frac{1}{2!}\sum_{s,s'=1}^{M}\left(\frac{\partial^2(\in_k + F_k - E_0^N)}{\partial Q_s \partial Q_{s'}}\right)_0 Q_s Q_{s'} \quad (52)$$

leads to a set of linear equations in the unknown normal coordinate shifts $\delta Q_{S'}$,

$$-\left(\frac{\partial(\in_k + F_k)}{\partial Q_s}\right)_0 = \sum_{s'\neq s}\left(\frac{\partial^2(\in_k + F_k)}{\partial Q_s \partial Q_{s'}}\right)_0 \delta Q_{s'},$$

$$+\left[\left(\frac{\partial^2(\in_k + F_k)}{\partial Q_3^2}\right)_0 - h\omega_s\right]\delta Q_s, s = 1 \ldots M, \quad (53)$$

where ω_s are frequencies of the reference molecule. The new coupling constants are then:

$$g_1 = \pm\left(1/\sqrt{2}\right)\left[\partial(\in_k + F_k)/\partial Q_l\right]_0 \quad (54)$$

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

Further it can be shown [65-67] that 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. (6). In second order one obtains:

$$\sum\nolimits_{\boldsymbol{k}}^{(2)}(\in) = \sum_{\substack{i,j\\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j\\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} \quad (58)$$

and the coupling constant $g_{l'}$ can be written as

$$g_l \approx \pm\frac{1}{\sqrt{2}}\frac{\partial \in_k}{\partial Q_l}\frac{1 + q_k(\partial/\partial\in)\sum_{\boldsymbol{k}}\left[-(V.I.P.)_k\right]}{1 - (\partial/\partial\in)\sum_{\boldsymbol{k}}\left[-(V.I.P.)_k\right]}, \quad (59)$$

where

$$q_k = \frac{\sum \frac{(V_{ksij} - V_{ksji})^2}{\left[-(V.I.P.)_k + \in_s - \in_i - \in_j\right]^2}\left[\frac{\partial \in_s}{\partial Q_l} - \frac{\partial \in_i}{\partial Q_l} - \frac{\partial \in_j}{\partial Q_l}\right]}{\frac{\partial \in_k}{\partial Q_l}\sum \frac{(V_{ksij} - V_{ksji})^2}{\left[-(V.I.P.)_k + \in_s - \in_i - \in_j\right]^2}} \quad (60)$$

It is suitable to use further the pole strength of the corresponding Green's function

$$\rho_k = \left\{1 - \frac{\partial}{\partial\in}\sum\nolimits_{\boldsymbol{k}}\left[-(V.I.P)_k\right]\right\}^{-1}; 1 \geq \rho_k \geq 0, \quad (61)$$

$$g_l \approx g_l^0\left[\rho_k + q_k(\rho_k - 1)\right], \quad g_l^0 = \pm 2^{-1/2}\partial \in_k / \partial Q_l \quad (62)$$

Below we firstly give the DFT definition of the pole strength corresponding to V. I. P.'s and confirm earlier data [65]: $p_k \approx 0,8$-0,95. The closeness of p_k to 1 in fact means that a role of the multi-body correlation effects is small ($g_l \approx g_l^0$).

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.:

$$(I.P.)_k = -\in_k - \sum_{j\notin,i\in F} \frac{\left(V_{kikj} - V_{kijk}\right)}{\in_j - \in_i} - \frac{1}{2} \sum_{\substack{i\in F \\ j,l\notin F}} \frac{\left(V_{kijl} - V_{kilj}\right)}{\in_k + \in_i - \in_j - \in_l} (1-\delta_k)$$

$$- \frac{1}{2} \sum_{\substack{p,q\in F \\ j\notin F}} \frac{\left(V_{kjpq} - V_{kjqp}\right)^2}{\in_k + \in_i - \in_p - \in_q} (1-\delta_p)(1-\delta_q) \qquad (64)$$

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

$$g_l \approx g_l^0 \left\{ 1 + \sum_{j\notin F} \frac{\left(V_{kkkj}\right)^2}{\left(\in_j - \in_k\right)^2} - \frac{1}{2} \left[\begin{array}{l} \displaystyle\sum_{\substack{i\in F \\ j,l\notin F}} \frac{\left(V_{kijl} - V_{kilj}\right)^2}{\left(\in_k + \in_i - \in_j - \in_l\right)^2} (1-\delta_k) + \\ \displaystyle + \sum_{\substack{p,q\in F \\ j,\notin F}} \frac{\left(V_{kjpq} - V_{kjqp}\right)^2}{\left(\in_k + \in_i - \in_p - \in_q\right)^2} (1-\delta_q)(1-\delta_p) \end{array} \right] \right\}$$

$$(65)$$

The second coupling constant can be written

$$\gamma_l = \gamma_l^0 \left(\frac{g_l}{g_l^0} \right) + \frac{1}{4} \sqrt{2} g_l^0 \frac{\partial}{\partial Q_l} \left(\frac{g_l}{g_l^0} \right) \qquad (66)$$

γ_l^0, is defined analogously g_l^0.

3. Quasiparticle Fermi-liquid DFT

In this chapter we present the quasiparticle Fermi-liquid version of the DFT theory, starting from the problem of searching for the optimal one-electron representation and following to refs. [60-68,111]. Two decades ago Davidson had pointed the principal disadvantages of the traditional representation based on the self-consistent field approach and suggested the optimal "natural orbitals" representation [22,23]. Nevertheless there remain insurmountable calculational difficulties in the realization of the Davidson program. One of the simplified recipes represents, for example, the Kohn-Sham DFT theory [40-42]. In ref. [111] the QED DFT version, based on the formally exact QED perturbation theory (PT), has been developed and a new approach to construction of the optimized one-quasiparticle representation has been proposed. In fact this approach is based on the energy approach, which is well known in the theory of radiative and non-radiative decay of the quasi-stationary states for multielectron systems. The energy approach uses the adiabatic Gell-Mann and Low formula [59] for the energy shift d*E* with electrodynamic scattering matrices. In a modern theory of molecules there is a number of tasks, where an accurate account for the complex exchange-correlation effects, including the continuum pressure, energy dependence of a mass operator etc., is critically important. It includes also the calculation of the vibration structure for the molecular systems. In this case it can be very useful the quasiparticle DFT [60]. In order to get the master equations and construct an optimal basis of the one-particle wave functions φ_λ one could use the Green's function method. Let us define the one-particle Hamiltonian for functions φ_λ so that the Greens' function pole part in the (φ_λ) representation is diagonal on λ. Starting equation is the Dyson equation for multi-electron (for example atom or molecule):

$$(\varepsilon - p^2/2 + \sum Z_\alpha / r_\alpha) \cdot G(x,x',\varepsilon) - \int dx' \sum(x,x',\varepsilon) = \delta(x-x')$$

$$(67)$$

where $x=(r,s)$ are the spatial and spin variables, $\sum$ is the mass operator; Z , as usually, a charge of a nucleus (nuclei) «α», G is the Green's function. In the representation of auxiliary functions $\varphi_\lambda^{\prime}$ the equation (67) has the following form:

$$(\varepsilon \cdot \delta_{\lambda\lambda_1} - [\frac{p^2}{2} - \sum \frac{Z_\alpha}{r_\alpha} + \sum(x,x',\varepsilon)]_{\lambda\lambda_1}) G_{\lambda\lambda'} = \delta_{\lambda\lambda'}$$

$$(68)$$

where λ_1 is an index of summation. It is natural to choose φ_λ so that the following expression will be diagonal:

$$[p^2/2 - \sum_\alpha Z_\alpha / r_\alpha + \sum(x,x',\varepsilon)]_{\lambda\lambda_1} = E_\lambda(\varepsilon) \cdot \delta_{\lambda\lambda_1}$$

$$(69)$$

$$G_{\lambda\lambda'} = G_\lambda \cdot \delta_{\lambda\lambda'}, G_\lambda = 1/[\varepsilon - E_\lambda(\varepsilon)] \qquad (70)$$

and the functions $\varphi_\lambda^{/}$, which diagonalizes G , satisfy to equation as follows: :

$$(p^2/2-\sum_\alpha Z_\alpha/r_\alpha)\varphi_\lambda^{/}(x,\varepsilon)+ \\ +\int\sum(x,x^{/},\varepsilon)\varphi_\lambda^{/}(x_1,\varepsilon)dx_1-E_\lambda(\varepsilon)\varphi_\lambda^{/}(x,\varepsilon) \quad (71)$$

One could introduce the mixed representation for a mass operator as follows:

$$\sum(x,p,\varepsilon)=\int\sum(x,x_1,\varepsilon)\exp[i(r-r_1)p]dr_1 \quad (72)$$

Then equation (71) with account for of the expression (72) can be written as follows:

$$[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon)]\varphi_\lambda^{/}(x,\varepsilon)= \\ =E_\lambda(\varepsilon)\varphi_\lambda^{/}(x,\varepsilon) \quad (73)$$

It can be shown that an operator $p=iv$ in (67) acts on functions which are on the right of $\sum(x,p,\varepsilon)$. So, in order to find the one-particle energies, defined by the pole part of the Green's function G, it is sufficient to know the functions $\varphi_\lambda^{/}$ under $\varepsilon=\varepsilon_\lambda$. The Greens' function pole part is as follows:

$$G_{\lambda\lambda^{/}}=a^\lambda\delta_{\lambda\lambda^{/}}/(\varepsilon-\varepsilon_\lambda+i\gamma_\lambda) \quad (74)$$

where

$$a^\lambda=1/(1-\partial E_\lambda/\delta\varepsilon)|_{\varepsilon=\varepsilon_\lambda},(\partial E/\partial\varepsilon)|_{\varepsilon=\varepsilon_\lambda}=(\partial E/\partial\varepsilon)|_{\lambda\lambda^{/}}$$

$$\varepsilon_\lambda=E_\lambda(\varepsilon)=\{p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon)\}|_{\lambda\lambda} \quad (75)$$

The functions $\varphi_\lambda^{/}(x)=\varphi_\lambda^{/}(x,\varepsilon_\lambda)$ are satisfying to following equation:

$$[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon_\lambda)]\varphi_\lambda=\varepsilon_\lambda\varphi_\lambda(x) \quad (76)$$

Introducing an expansion for self-energy part $\sum$ into set on degrees $x,\varepsilon-\varepsilon_F,p^2-p_F^2$ (here ε_F and p_F are the Fermi energy and pulse correspondingly):

$$\sum(x,p,\varepsilon)=\sum{}_0(x)+(\partial\sum/\partial p^2)(p^2-p_F^2)+ \\ +(\partial\sum/\partial\varepsilon)(\varepsilon-\varepsilon_F)+...$$

then equation (76) is rewritten as follows:

$$[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum{}_0(x)+p(\partial\sum/\partial p^2)p]\Phi_\lambda(x)= \\ =(1-\partial\sum/\partial\varepsilon)\varepsilon_\lambda\Phi_\lambda(x) \quad (77)$$

The functions Φ_λ in (77) are orthogonal with a weight $r_k^{-1}=a^{-1}=[1-\partial\sum/\partial\varepsilon]$. Now one can introduce the wave functions of the quasiparticles $\varphi_\lambda=a^{-1/2}\Phi_\lambda$, which are, as usually, orthogonal with weight 1. For complete definition of $\{\varphi_\lambda\}$ it should be determined the values $\sum{}_0,\partial\sum/\partial p^2,\partial\sum/\partial\varepsilon$. Naturally, the equations (77) can be obtained on the basis of the variational principle, if we start from a Lagrangian of a system L_q (density functional). It should be defined as a functional of the following quasiparticle densities:

$$\nu_0(r)=\sum_\lambda n_\lambda|\Phi_\lambda(r)|^2, \\ \nu_1(r)=\sum_\lambda n_\lambda|\nabla\Phi_\lambda(r)|^2, \\ \nu_2(r)=\sum_\lambda n_\lambda[\Phi_\lambda^*\Phi_\lambda-\Phi_\lambda^*\Phi_\lambda]. \quad (78)$$

The densities ν_0 and ν_1 are similar to the HF electron density ρ ($\rho=\nu\cdot a$) and kinetical energy density correspondingly; the density ν_2 has no an analog in the HFock or standard Kohn-Sham theory and appears as result of account for the energy dependence of the mass operator $\sum$. Lagrangian L_q can be written as 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:

$$L_q^0 = \int dr \sum_{\lambda} n_{\lambda} \Phi_{\lambda}^{*} (i\partial / \partial t - \varepsilon_p) \Phi_{\lambda}, \quad (79)$$

And an interaction Lagrangian is defined in the form, which is characteristic for a standard (Kohn-Sham) density functional theory (as a sum of the Coulomb and exchange-correlation terms), however, it takes into account for the energy dependence of a mass operator $\sum$:

$$L_q^{\text{int}} = L_K - \frac{1}{2} \sum_{i,k=0}^{2} \int \beta_{ik} F(r_1, r_2) \nu_i(r_1) \nu_k(r_2) dr_1 dr_2 \quad (80)$$

where β_{ik} are some constants (look below), F is an effective potential of the exchange-correlation interaction. Let us explain here the essence of the introduced constants. Indeed, in some degree they have the same essence as similar constants in well-known Landau Fermi liquid theory and Migdal finite Fermi-systems theory. The Coulomb interaction part L_K looks as follows:

$$\begin{aligned} L_K = -\frac{1}{2} \int [1 - \textstyle\sum_2 (r_1)] \nu_0 (r_1) [1 - \\ - \textstyle\sum_2 (r_2)] \nu_0 (r_2) / | r_1 - r_2 | dr_1 dr_2 \end{aligned} \quad (81)$$

where $\sum_2 = \partial \sum / \partial \varepsilon$. Regarding the exchange-correlation potential *F*, it should be noted the there are many possible approximations (directly in the DFT and its modern generalizations). Earlier in our atomic and molecular theories we use the following form:

$$\begin{aligned} F(r_1, r_2) = X(\int dr \rho_c^{(0)1/3}(r) / |r - r_1| |r - r_2| - \\ -(\int dr' \rho_c^{(0)1/3}(r') / |r_1 - r'| \cdot \\ \cdot \int dr'' \rho_c^{(0)1/3}(r'') / |r'' - r_2|) / < \rho_c^{(0)1/3} > \\ < \rho_c^{(0)1/3} > = \int dr \rho_c^{(0)1/3}(r) \end{aligned} \quad (82)$$

where X is the numerical coefficient. It has been obtained in the refs. [74-76] on the basis of calculating the Rayleigh-Schrödinger perturbation theory Feynman diagrams of the second and higher order (so called polarization diagrams) in the Thomas-Fermi approximation. The corresponding relativistic generalization of the potential (82) looks as follows [76]:

$$\begin{aligned} F_{pol}^{d}(r_1 r_2) = X(\int dr' \rho_c^{(0)1/3}(r') \theta(r') / |r_1 - r'| |r' - r_2| - \\ -(\int dr' \rho_c^{(0)1/3}(r') \theta(r') / |r_1 - r'| | \int dr'' \rho_c^{(0)1/3}(r'') \theta(r'') / \\ / |r'' - r_2|) / < \rho_c^{(0)1/3} >); \\ < \rho_c^{(0)1/3} > = \int dr \rho_c^{(0)1/3}(r) \theta(r) \end{aligned} \quad (83)$$

where , c is the light velocity.

Another alternative expression has been introduced by Victor- Laughlin-Taylor (c.f. refs. [24,25]):

$$\begin{aligned} F(\vec{r}_1, \vec{r}_2) = \frac{1}{r_{12}} - \frac{\alpha_d}{r_1^2 r_2^2} p_1 (\cos\theta_{12}) w_3 (r_2 / r_0) w_3 (r_2 / r_0) - \\ - \frac{\alpha_d'}{r_1^3 r_2^3} p_2 (\cos\theta_{12}) w_4 (r_1 / r_0) w_4 (r_2 / r_0) \end{aligned} \quad (84)$$

where p_1 are the Legander polynomials, $\cos\theta_{12} = \vec{r}_1 \vec{r}_2 (r_1 r_2)$. In the local density approximation in the density functional the potential *F* can be expressed through the exchange-correlation pseudo-potential V_{XC} as follows [41,42]:

$$F(r_1, r_2) = \delta V_{XC} / \delta \nu_0 \cdot \delta(r_1 - r_2). \quad (85)$$

Further, one can get the following expressions for $\sum_i = -\delta L_q^{\text{int}} / \delta \nu_1$:

$$\begin{aligned} \textstyle\sum_0 = (1 - \textstyle\sum_e) V_K + \textstyle\sum_0^{ex} + \\ + \frac{1}{2} \beta_{00} \delta^2 V_{XC} / \delta \nu^2 \cdot \nu_0^2 + \beta_{00} \delta V_{XC} / \delta \nu_0 \cdot \nu_0 + \\ + \beta_{01} \delta V_{XC} / \delta \nu_0 \cdot \nu_1 + \beta_{01} \delta^2 V_{XC} / \delta \nu_0^2 \cdot \nu_0 \nu_1 + \\ + \beta_{02} \delta^2 V_{XC} / \delta \nu_0^2 \cdot \nu_0 \nu_2 + \beta_{02} \delta V_{XC} / \delta \nu_0 \cdot \nu_2 \\ \textstyle\sum_1 = \beta_{01} \delta V_{XC} / \delta \nu_0 \cdot \nu_0 + \beta_{12} \delta V_{XC} / \delta \nu_0 \cdot \nu_2 + \\ + \beta_{11} \delta V_{XC} / \delta \nu_0 \cdot \nu_1; \\ \textstyle\sum_2 = \beta_{02} \delta V_{XC} / \delta \nu_0 \cdot \nu_0 + \beta_{12} \delta V_{XC} / \delta \nu_0 \cdot \nu_1 + \\ + \beta_{22} \delta V_{XC} / \delta \nu_0 \cdot \nu_2; \end{aligned} \quad (86)$$

Here V_K is the Coulomb term (look above), $\sum_0^{ex}$ is the exchange term. Using the known canonical relationship:

$$H_q = \Phi_{\lambda}^{*} \delta L_q / \delta \Phi_{\lambda}^{*} + \Phi_{\lambda} \delta L_q / \delta \Phi_{\lambda} - L_q$$

after some transformations one can receive the expression for the quasiparticle Hamiltonian, which is corresponding to a Lagrangian L_q:

$$
\begin{aligned}
&H_q = H_q^0 + H_q^{\mathrm{int}} = H_q^0 - L_K + \\
&+\frac{1}{2}\beta_{00}\delta V_{XC}/\delta\nu_0\cdot\nu_0^2 + \\
&+\beta_{01}\delta V_{XC}/\delta\nu_0\cdot\nu_0\cdot\nu_1 + \frac{1}{2}\beta_{11}\delta V_{XC}/\delta\nu_0\cdot\nu_1^2 - \\
&-\frac{1}{2}\beta_{22}\delta V_{XC}/\delta\nu_0\cdot\nu_2^2
\end{aligned}
\qquad (87)
$$

Further let us give the corresponding comments regarding the constants b_{ik}. First of all, it is obvious that the terms with constants $\beta_{01}, \beta_{11}, \beta_{12}, \beta_{22}$ give omitted contribution to the energy functional (at least in the zeroth approximation in comparison with others), so they can be equal to zero. The value for a constant β_{00} in some degree is dependent upon the definition of the potential V_{xc}. If as V_{xc} it is use one of the correct exchange-correlation potentials from the standard density functional theory, then without losing a community of statement, the constant β_{00} can be equal to 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 atomic or molecular system (it is usually defined from the ionization cross-sections) [60]:

$$
F_{sp} = \left\{1 - \frac{\partial}{\partial \in}\sum{}_{kk}\left[-(V.I.P.)_k\right]\right\} \qquad (88)
$$

The term $\partial\sum/\partial\varepsilon$ is defined above. It is easily to understand the this definition is in fact corresponding to the pole strength of the corresponding Green's function [62].

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 [40-42]:

$$
V_{XC}(r) = f(\theta)V_X(r) - 0{,}0333\cdot\ln[1 + 18{,}376\cdot\rho^{1/3}(r)] \qquad (89)
$$

where $V_X = -(1/\pi)[3\pi^2\cdot\rho(r)]^{1/3}$

is the Kohn-Sham exchange potential, $\theta = [3\pi^2\rho]^{1/3}/c$, and function $f(\theta)$ is as follows:

$$
f(\theta) = 3\ln[\theta + (\theta^2+1)^{1/2}]/[2\theta(\theta^2+1)^{1/2}] - 1/2 \qquad (90)
$$

Using the above written formula, one can simply define values (61), (88). As example in table 1 we present our calculational data for spectroscopic factors of some atoms together with available experimental data and results, obtained in the Hartree-Fock theory plus random phase approximation.

Further, let us give a short comment regarding an universality of the constants b_{ik}. From the point of view of the analogous universality of the constants in the well-known Landau Fermi-liquid theory and Migdal finite Fermi-systems theory [62]. Indeed, as we know now, the entire universality of the constants in the last theories is absent, though a range of its changing is quite little. Without a detailed explanation, we note here that the corresponding constants in our theory possess the same universality as ones in the Landau Fermi-liquid theory and Migdal finite Fermi-systems theory. More detailed explanation requires a careful check. Further it is obvious that omitting the energy dependence of the mass operator (i.e. supposing $\beta_{02} = 0$) the quasiparticle density functional theory can be resulted in the standard Kohn-Sham theory.

Note: $F_{\exp}^{*}$ - experimental value of spectroscopic factor; $\widetilde{F}_{RPA}$ is the value, obtained in the random phase approximation with exchange.

In this essence the presented approach to definition of the functions basis $\{\Phi_\lambda\}$ of a Hamiltonian H_q can be treated as an improved in comparison

Table 1
Spectroscopic factors of the external ns^2 shells of some atoms and ions

Atom, ion	Терм	N	F_{sp}	$F^*_{\exp}$ $\widetilde{F}_{RPA}$
Ar	1_S	3	0,60	0,56 0,70
TI $^{(IV)}$	1_S	3	0,50	0,34 0,60
Xe	1_S	5	0,36	
TI	2_P	6	0,36	
Pb$^+$	2_P	6	0,33	
Pb	3_P	6	0,34	
Pb	1_D	6	0,34	
Pb	1_S	6	0,34	
Bi$^+$	3_P	6	0,32	
Bi	4_S	6	0,33	
Bi	2_D	6	0,33	
Bi	2_P	6	0,33	
Po$^+$	4_S	6	0,31	
Po	3_P	6	0,31	
Po	1_D	6	0,31	
Po	S 1	6	0,31	
As$^+$	3_P	6	0,30	
As	2_P	6	0,30	
As$^-$	1_S	6	0,31	
Rn$^+$	2_P	6	0,29	
Rn	1_S	6	0,29	
Fr$^+$	1_S	6	0,28	
Fr	2_S	6	0,28	
Ra	1_S	7	0,43	
Ac	2_D	7	0,41	
Ac	2_F	7	0,42	
Th	3_H	7	0,41	
Th	3_F	7	0,42	
Pa	4_I	7	0,42	
U	5_L	7	0,42	

with similar basises of other 1-particle representations (HF, Hatree-Fock-Slater, Kohn-Sham etc.). Naturally, this advancement can be manifested during studying those properties of the multi-electron systems, when accurate account for complex exchange-correlation effects, including continuum pressure, energy dependence of mass operator etc., is critically important.

4. The application of the combined Green's function method and quasiparticle DFT approach to diatomics

We choose the diatomic molecules of N_2, CO (and some others) for application of the combined Green's function method and quasiparticle DFT approach. In ref. [65] it has been shown that the diatomics spectra can be in principle reproduced by applying a one-particle theory with account of the correlation and reorganization effects. The corresponding coupling constants depend on the balance of these effects. The nitrogen molecule has been naturally discussed in many papers. The valence V. I. P. 's of N_2 have been calculated [61,62,65] 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.

In 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 calculation of Cade *et al.*[71,72] one finds that including reorganization the V. I. P. 's assigned by σ_g and σ_u improve while for the 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. The above-mentioned Green's functions calculation which takes account of reorganization and correlation effects leads to the experimental sequence of V. I. P.'s. In Table 2 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's functions and DFT approach (e) and corresponding pole strengths (d,e) are listed.

Table 2

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	Exp VIP a	$-\in_k^b$	$-(\in_k+R_k)^c$	Calc^d V.I.P.'s	ρ_k^d	Calc^e V.I.P.'s	ρ_k^e
3 σ_g	15,6	17,4	16,0	15,5	0,9	15,5	0,9
1 π_u	16,9	17,1	15,7	16,8	0,9	16,8	0,9
2 σ_u	18,8	20,9	19,9	18,6	0,9	18,6	0,8

Therefore, the results, obtained within the Green functions approach and combined method are very much close. Taking into account a simplification of the calculational procedure within the DFT approach, the generalized Cederbaum et al theory looks more attractive else. As it's known, of the three bands in the experimental low-energy spectrum of N_2 molecule (Fig. 3), only the $1\pi_u$ band exhibits a strong vibrational structure.

When a change of frequency due to ionization is small, the density of states can be well approximated using only one parameter *g:*

$$N_k(\in)=\sum_{n=0}^{\infty} e^{-s}\frac{S^n}{n!}\delta(\in-\in_k+\Delta\in_k+n\cdot\hbar\hat{\omega}),$$
$$S=g^2(\hbar\omega)^{-2} \qquad (70)$$

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.3 the experimental and calculated photoelectron spectra for the N_2.molecule are presented. The uppermost spectrum is calculated with S^0 (i.e. the constant S calculated with g^0) and Eq. (70) [13]. The middle spectrum is calculated with values of S from Eq. (62).

It is important to note that the original Green's functions and combined Green functions +DFT approach coincide in the scale of the figure. In a whole the agreement between the calculated spectrum (corrected *g*) and the experimental one is improved. As another example, the molecule CO can be considered.

The experimental and calculated photoelectron spectra for CO molecule are listed in Fig.4. One can see quite physically reasonable agreement between experiment and theory. The original Green's functions [13] and combined Green's functions +DFT approach practically coincide. On inclusion of the anharmonicites it should be mentioned that a theory can be generalized by means a standard normal coordinate expansion of Hamiltonian to third and higher orders and correspondingly the theory of the density of states functions N_k developed above can easily be generalized too.

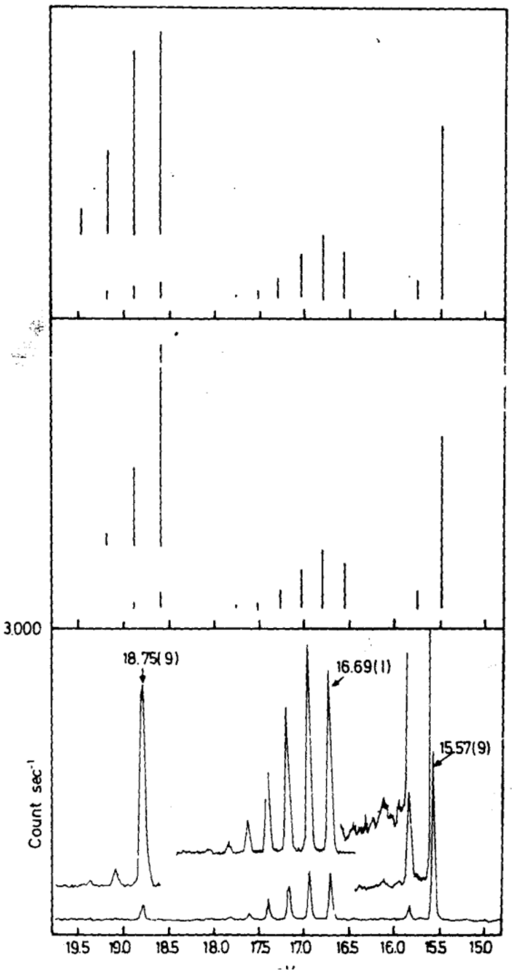

Figure 3. Experimental [65]and calculated PE spectra N_2; Uppermost spectrum is calculated with S^0 and Eq. (70). The middle spectrum is calculated with S values from (62) (see text).

5. Summary

We present a new combined theoretical approach to vibrational structure in photo-electron spectra of molecules, which is based on the Green's function method and DFT.

In fact approach presented generalizes the standard Green's function approach [65-68]. 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. It is important that the calculational procedure is significantly simplified with using the quasiparticle DFT formalism.

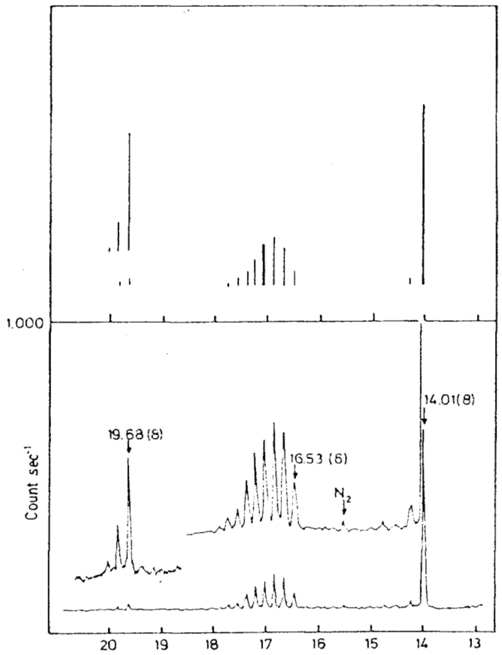

Figure 4. The experimental [65] and calculated photoelectron spectra of CO. The upper spectrum is calculated with S^0 and Eq. (70) (see text).

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THE GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRON SPECTRA OF MOLECULES: REVIEW OF METHOD

Abstract. We present the basis's of the new combined theoretical approach to vibrational structure in photoelectron spectra of molecules. The approach is based on the Green's function method, which generalizes the Cederbaum-Domske formalism, and quasiparticle density functional theory. It generalizes the known Green's function approach by It is presented a new procedure for determination of the density of states, which describe the vibrational structure in molecular photoelectron spectra.

Key words: density functional theory, Green's function method, photoelectron spectra

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МЕТОД ФУНКЦИЙ ГРИНА И ТЕОРИЯ ФУНКЦИОНАЛА ПЛОТНОСТИ ДЛЯ ОПРЕДЕЛЕНИЯ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ В ФОТОЭЛЕКТРОННЫХ СПЕКТРОВ МОЛЕКУЛ: ОБЗОР МЕТОДА

Резюме

Изложены основы нового комбинированного теоретического подхода к определению колебательной структуры в фотоэлектронных спектрах молекул. Подход основан на квазичастичном методе функций Грина, обобщающем формализм Цедербаума-Домске, и квазичастичной теории функционала плотности. Приведена процедура вычисления плотности состояний, описывающей колебательную структуру в молекулярных фотоэлектронных спектрах.

Ключевые слова: теория функционала плотности, метод функций Грина, фотоэлектронные спектры.

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О. В. Глушков

МЕТОД ФУНКЦІЙ ГРІНА І ТЕОРІЯ ФУНКЦІОНАЛА ГУСТИНИ ДЛЯ ВИЗНАЧЕННЯ КОЛИВАЛЬНОЇ СТРУКТУРИ У ФОТОЕЛЕКТРОННИХ СПЕКТРАХ МОЛЕКУЛ: ОГЛЯД МЕТОДУ

Резюме

Викладені основи нового комбінованого теоретичного підходу до визначення коливальної структури в фотоелектронних спектрах молекул. Підхід заснований на квазічастинковом методі функцій Гріна, що узагальнює формалізм Цедербаума-Домске, і квазічастинковій теорії функціонала густини. Наведена процедура обчислення густини станів, яка описує коливальну структуру в молекулярних фотоелектронних спектрах.

Ключові слова: теорія функціонала густини, метод функцій Гріна, фотоелектронні спектри