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SPECTROSCOPIC FACTORS OF DIATOMIC MOLECULES: OPTIMIZED GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL METHOD

It is presented an advanced approach to computing the spectroscopic factors of the diatomic molecules, which is based on the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach. The Fermi-liquid quasiparticle version of the density functional theory is modified and used. The density of states, which describe the vibrational structure in photoelectron spectra, is defined with the use of combined DFT-GF approach and is well approximated by using only the first order coupling constants in the optimized one-quasiparticle approximation. Using the combined DFT-GF approach to computing the spectroscopic factors of diatomic molecules leads to significant simplification of the calculation procedure and increasing an accuracy of theoretical prediction.

1. Introduction

In this paper we study the problem of calculating the important spectroscopic characteristics of multielectron systems (atoms and molecules), namely, the spectroscopic factor. The spectroscopic factor is one of the most important characteristics of atomic and molecular systems and the precise information about it is very important for many applications [1-38]. The theoretical determination of spectroscopic factor for multielectron atomic and molecular systems is a rather complicated task, since in the framework of traditional a priori methods it is reduced to a calculation of corrections of perturbation theory of the type:

$$\sum_{i} \left|Vij\right|^{2}/(\varepsilon_{i}-\varepsilon_{j})$$

with summation over a large number of intermediate states. The spectroscopic factor is usually experimentally determined using inelastic scattering of fast electrons, as well as photoelectron spectroscopy (see [1]). In this case, as a rule, there is a discrepancy between the results of measurements of spectroscopic factors in these experiments caused by the influence of many electronic correlations in the initial state of the multielectron system

In this paper we present an advanced approach to computing the spectroscopic factors of the diatomic molecules within the hybrid combined density functional theory (DFT) in the Fermi-liquid formulation and the Green's-functions (GF) approach to quantitative determination of the spectroscopic factors for some molecular systems. The approach is based on the Green's function method (Cederbaum-Domske version) [1,2] and Fermi-liquid DFT formalism [3-7] and using the novel effective density functionals (see also [11-22]). It is important that the calculational procedure is significantly simplified with using the quasiparticle DFT formalism.

As usually (see details in refs. [1,4,7]), 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:

$$N_{k}(\epsilon)=(1/2\pi\hbar)\int dte^{i\hbar^{-1}\epsilon t}\langle\psi_{0}|\mathrm{a}_{k}^{t}(0)a_{k}(t)|\psi_{0}\rangle\,, \quad (1)$$

where $|\Psi_0\rangle$ is the exact ground state wave function of the reference molecule and $a_k(t)$ is an electron destruction operator, both in the Heisenberg picture.

2. Theory: Density of states in one-body and many-body solution

As usually, introducing a field operator $\Psi(R,\theta,x) = \sum_i \phi_i(x,R,\theta)a_i(R,\theta)$ with the Hartree-Fock (HF) one–particle functions ϕ_i ($\in_i (R)$ are the one-particle HF energies and f denotes the set of orbitals occupied in the HF ground state; R_0 is the equilibrium geometry on the HF level) and dimensionless normal coordinates Q_s one can write the standard Hamiltonian as follows [2,7]:

$$H = H_E + H_N + H_{EN}^{(1)} + H_{EN}^{(2)}, \qquad (3)$$

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

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

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

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

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

$$Q_s = (1/\sqrt{2})(\, b_s + b_s^t)$$
$$\partial/\partial Q_s = (1/\sqrt{2})(\, b_s - b_s^t)\,. \qquad (4)$$

The interpretation of the above Hamiltonian and an exact solution of the one-body HF problem is given in refs. [1,-7]. The usual way is to define the HF-single-particle component H_0 of the Hamiltonian (4) is as in Refs. [1,4]. Correspondingly in the one-particle picture the density of occupied states is given by

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(\epsilon-\epsilon_k)t}\langle 0|\; e^{\pm i\hbar^{-1}\widetilde{H}_{0}t}\,|0\rangle, \qquad (5)$$

$$\widetilde{H}_0 = \sum_{s=1}^{M} \hbar\omega_s b_s^t b_s + \sum_{s=1}^{M} g_s^k (b_s + b_s^t) + \qquad (6)$$
$$+ \sum_{s,s'=1}^{M} \gamma_{ss'}^k (b_s + b_s^t)(b_{s'} + b_{s'}^t)$$

$$g_s^i = \pm\frac{1}{\sqrt{2}}\left(\frac{\partial^{o}{}_i}{\partial Q_s}\right)_0, \quad \gamma_{s\,'}^i = \pm\frac{1}{4}\left(\frac{\partial^{2\,o}{}_i}{\partial Q_s \partial Q_{s'}}\right)_0 .(7)$$

To get function $N_k({}^{o})$ one calculates the GF $G_{k\,'}({}^{o})$ (see details in Refs. [1-7,31-35]:

$$G_{kk\,'}({}^{o}) = -i\hbar^{-1}\int_{-\infty}^{\infty} dt e^{i\hbar^{-1}} \langle\psi_0|\; \grave{O}\{\; a_k(t)a_k^t(0)\;\}\; |\psi_0\rangle \qquad (8)$$

Choosing the unperturbed H_0 to be $H_0 = \sum {}^{o}{}_i a_i^t a_i + H_N$ one could define GF as

$$G_{kk'}^{\theta}(t) = \pm\delta_{kk'} i \exp\left[- \dot{n}^{\;-1}\left(\varepsilon_k \mp \Delta\varepsilon\right)t\right]\cdot$$
$$\cdot\sum_n \left|\left\langle \hat{n}_k \middle| U_k \middle| 0\right\rangle\right|^2 \exp\left(\pm\, \dot{n}_{\;k}\cdot\hat{\omega}_k t\right) \qquad , (9)$$

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

The zeros of the functions:

$$D_k(\in) \in\; -\left[\in^{p} + \Sigma(\in)\right]_k, \qquad (10)$$

where $\left(\in^{\varphi} + \Sigma\right)_k$ denotes the k-th eigenvalue of the diagonal matrix of the one-particle energies added to matrix of the self-energy part, are the negative V. I. P. ‘s for a given geometry. One can write [2,4]:

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

$$F_k = \Sigma_{\boldsymbol{k}}\left(-\left(V.I.P.\right)_k\right) \approx \frac{1}{1-\partial\Sigma_{\boldsymbol{k}}\left(\in_k\right)/\partial_{\in}}\Sigma_{\boldsymbol{k}}\left(\in_k\right) \quad . \tag{11}$$

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

$$g_1 = \pm\left(1/\sqrt{2}\right)\left[\partial\left(\in_k + F_k\right)/\partial Q_l\right]_0 \tag{12}$$

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

The coupling constants g_l, $y_{ll'}$ are calculated by the well-known perturbation expansion of the self-energy part. One could write:

$$\sum\nolimits_{\boldsymbol{k}}^{(2)}\left(\in\right) = \sum_{\substack{i,j \\ s\notin F}} \frac{\left(V_{ksij} - V_{ksji}\right)V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s\notin F}} \frac{\left(V_{ksij} - V_{ksji}\right)V_{ksij}}{\in + \in_s - \in_i - \in_j} \tag{13}$$

and the coupling constant $g_{l'}$ are as [17]:

$$g_l \approx \pm\frac{1}{\sqrt{2}}\frac{\partial \in_k}{\partial Q_l}\frac{1 + q_k\left(\partial/\partial\in\right)\sum_{\boldsymbol{k}}\left[-\left(V.I.P.\right)_k\right]}{1 - \left(\partial/\partial\in\right)\sum_{\boldsymbol{k}}\left[-\left(V.I.P.\right)_k\right]} \tag{14}$$

The pole strength of the corresponding GF:

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

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

$$g_l^0 = \pm 2^{-1/2}\partial\in_k/\partial Q_l \tag{15}$$

3. Fermi-liquid quasiparticle density functional theory

The quasiparticle Fermi-liquid version of the DFT [3-8,31,36] is used to determine the coupling constants etc. The master equations can be obtained on the basis of variational principle, if we start from a Lagrangian of a molecule L_q. It should be defined as a functional of quasiparticle densities:

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

$$\nu_1(r) = \sum_\lambda n_\lambda\,|\nabla\Phi_\lambda(r)|^2, \tag{16}$$

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

The densities υ_0 and υ_1 are similar to the HF electron density and kinetical energy density correspondingly; the density υ_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 the interaction Lagrangian is defined in the form, which is characteristic for a standard DFT (as a sum of the Coulomb and exchange-correlation terms), but, it takes into account for a mass operator energy dependence of Σ :

$$L_q^{\text{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2}\int \beta_{ik}F(r_1,r_2)\nu_i(r_1)\nu_k(r_2)dr_1dr_2 \tag{17}$$

where F is an effective exchange-correlation interaction potential. The constants β_{ik} are defined in Refs. [3-5]. The constant β_{02} can be calculated by analytical way, but it is very useful to keep in mind its connection with a spectroscopic factor F_{sp} [4,5]:

$$F_{sp} = \left\{1 - \frac{\partial}{\partial\in}\sum\nolimits_{\boldsymbol{k}}\left[-(V.I.P.)_k\right]\right\} \tag{18}$$

The new element is linked with using the DFT correlation Gunnarsson-Lundqvist, Lee-Yang-Parrr functionals (c.g.[12-16]).

4. Results and conclusions

Below we present the results of calculation of the spectroscopic factors for a number of diatomic molecules, in particular, C_2, N_2, O_2, F_2 in the ground state, as well as dimers of noble gases Ar_2^*, Kr_2^*, Xe_2^* in the lowest excited state. As the input data, the data obtained in the HF approximation [2,40] are used. For the C_2, N_2, O_2, F_2 the following spectroscopic factors were obtained for core (F_p^c) and valence (F_p^V) shells:

$$C_2 - F_{sp}^c = 0.49, F_{sp}^v = 0.80,$$

$$N_2 - F_{sp}^c = 0.46, F_{sp}^v = 0.77,$$

$$O_2 - F_{sp}^c = 0.43, F_{sp}^v = 0.74,$$

$$F_2 - F_{sp}^c = 0.39, F_{sp}^v = 0.71.$$

The obtained values of spectroscopic factors make it possible to assess to a certain extent the role of various types of correlations, in particular, intra-core and intra-valent, in these molecules. Since the spectroscopic factor, by its definition, is related to the dependence of the MSS on energy not taken into account in the HF approximation (always in this approximation: $F_p = 1$), the difference F_p from 1 indicates the corresponding role of various correlation effects. In particular, for these molecules, the contribution of intra-core correlations is somewhat more significant than that of intra-valent ones, which is also confirmed in ab initio calculations (c.f., [40]). For noble gas dimers ($n\delta_g^2$ outer shells) F_p^n are calculated:

$$Ar_2^* - F_{sp}^4 = 0{,}58 - (R_e = 7.1\text{a.u.}),$$

$$Kr_2^* - F_{sp}^7 = 0.37 - (R_e = 7.6\text{a.u.}),$$

$$Xe_2^* - F_{sp}^{10} = 0.26 - (R_e = 8.2\text{a.u.})$$

An analysis of the data indicates presence of strong correlation effects for the molecules, a number of features in the photoionization cross section of the $n\delta^2$ shells, namely, the possible collectivization of the $n\delta^2{}_g$ shells, the presence of "shadow" states in the molecules with which strong mixing takes place and to which the strength of the initial level $(1 - F_p)$ is transmitted. Note that such effects are known in the theory of atomic photoelectric effect, namely, for noble gas atoms (Ar and others) [6,41]).

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Summary. It is presented an advanced approach to computing the spectroscopic factors of the diatomic molecules, which is based on the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach. The Fermi-liquid quasiparticle DFT version is modified and used. The density of states, which describe the vibrational structure in photoelectron spectra, is defined with the use of combined DFT-GF approach and is well approximated by using only the first order coupling constants in the optimized one-quasiparticle approximation. Using the combined DFT-GF approach leads to significant simplification of calculation procedure and increasing an accuracy of theoretical prediction.

Key words: diatomic molecules, Green's functions, density functional

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СПЕКТРОСКОПИЧЕСКИЕ ФАКТОРЫ ДЛЯ ДВУХАТОМНЫХ МОЛЕКУЛ: ОПТИМИЗИРОВАННЫЙ МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ

Резюме. Представлен усовершенствованный подход к вычислению спектроскопических факторов двухатомных молекул, базирующийся на гибридной комбинированной теории функционала плотности (ТФП) и методе функций Грина (ФГ). Используется модель ферми-жидкостная квазичастичная версия ТФП. Плотность состояний, которая описывает колебательную структуру в фотоэлектронных спектрах, определяется с использованием комбинированного подхода ТФП - ФГ. Использование комбинированного ТФП-ФГ подхода приводит к значительному упрощению процедуры расчета и повышению точности теоретического прогнозирования.

Ключевые слова: двухатомные молекулы, функция Грина, функционал плотности

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СПЕКТРОСКОПІЧНІ ФАКТОРИ ДВОАТОМНИХ МОЛЕКУЛ: ОПТИМІЗОВАНИЙ МЕТОД ФУНКЦІЙ ГРІНА І ФУНКЦІОНАЛУ ГУСТИНИ

Резюме. Представлений вдосконалений метод обчислення спектроскопічних факторів 2-атомних молекул, що базується на гібридній теорії функціонала щільності (ТФП) і методі функцій Гріна (ФГ). Використано фермі-рідинну квазічастинкову версію ТФП. Густина станів, які описує коливальну структуру фотоелектронного спектру, визначається в межах ТФП-ФГ методу. Використання комбінованого ТФП-ФГ методу призводить до спрощення процедури обчислень, підвищення точності прогнозу.

Ключові слова: двоатомні молекули, функція Гріна, функціонал густини