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DENSITY FUNCTIONAL AND GREEN'S FUNCTIONS METHOD TO COMPUTING SPECTRAL PARAMETERS OF DIATOMIC MOLECULES

It is presented a new effective method of calculating the energy and spectral parameters of diatomic molecules based on the hybrid theory of the quasi-particle density functional and the theory of Green's functions. As an illustration, the data of the calculation of the vertical ionization potentials and the coupling constants (vibrational structure) of the photoelectron spectra of a number of diatomic molecules, in particular, N_2, are received. It is presented a detailed comparison of the received results with the data of standard theories of the Hartree-Fock type, the multi-configuration electron propagator method, and the extended theory based on Koopmans' theorem using multi-configurational self-consistent field wave functions with different sets of basis functions. Iit is shown that the consistent, maximally precise consideration of exchange-correlation effects and reorganization effects within the framework of the combined theory leads to a rather significant improvement in the agreement of theoretical and experimental data both in terms of ionization potentials and photoelectron spectra in general..

1. Introduction

Currently, the optics and spectroscopy of ordinary molecular, as well as combined and hybrid photon-atom-molecular systems, and, as a part of it, photoelectron spectroscopy (PES), belong to one of the directions of modern optics and spectroscopy, which are intensively developing, which, firstly, is associated with the use of fundamentally new methods and technologies in relevant experimental research, in particular, based on new powerful sources of laser radiation, and secondly, with the sharply increasing theoretical and applied value of relevant data regarding energy and spectral properties of ordinary molecular (diatomic and polyatomic molecules), as well as combined and hybrid photon-atom-molecular systems, that is, molecules in the field of intense electromagnetic radiation for numerous physical and other applications and applications [1-28]. Modern molecular optics and spectroscopy has in its theoretical and computational arsenal a rather huge number of diverse theoretical approaches to the calculation of energy and spectroscopic characteristics of molecules (ionization and excitation potentials, spectra of excited states, potential energy curves, spectroscopic molecular steels, dipole moments, parameters of the vibrational and rotational structure of the spectra, etc.). Among them, such well-known powerful and consistent approaches as self-consistent field methods of the Hartree-Fock-Rothaan (HFR), Hartree-Fock-Slater (HFS), X ✔ -method, in multi- and even mega-configurational versions should be especially noted and highlighted, the density functional method (DFT) in numerous implementations, the Green's function method (GF), coupled-cluster theories (CCT), the valence bond method (RCI-VB) with configuration interaction and various versions formalism of perturbation theory (RT), etc.

In this paper we present new effective method of calculating the energy and spectral parameters of diatomic molecules based on the hybrid theory of the quasi-particle density functional and the theory of Green's functions [1,9-11]. As an illustration, the data of the computing vertical ionization potentials and

the coupling constants (vibrational structure) of the photoelectron spectra of a number of diatomic molecules, in particular, N_2, are given, and a detailed comparison of some available data. The approach is based on the Green's function method (Cederbaum-Domske and Khetselius versions) [2-4] and Fermi-liquid DFT formalism [5-8].

2. Combined Green's functions and Fermi-liquid quasiparticle density functional theory

As the key moments of the combined method have been presented in Refs. [1,9-11], here we concern only such a points, which are important for computing vertical ionization potentials and the coupling constants (vibrational structure) of the photoelectron spectra of diatomic molecules. According to [1,2, 9] the molecular Hamiltonian van be written in the following form as follows:

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

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

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

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

$$\cdot + \frac{1}{4} \sum_i \sum_{s'=1}^{M} \left(\frac{\partial^2 \epsilon_i}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t)[a_i^t a_i - n_i], \qquad (3)$$

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

$$+ \frac{1}{8} \sum_{s,s'=1}^{M} \sum \left(\frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s''}} \right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t) \cdot$$
$$[\delta v_1 a_i^t a_j^t a_k + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t] \qquad (4)$$

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; $\in_i(R)$ 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); the ω_s are the HF frequencies; b_s, b_s^t are destruction and creation operators for vibrational quanta, Q_s are dimensionless normal coordinates are as follows:

The usual way is to define the HF-single-particle component H_0 of the Hamiltonian (4) is as in Refs. [1,2]. Correspondingly in the one-particle picture the density of occupied states is given by

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(\epsilon - \epsilon_k)t} \langle 0| e^{\pm i\hbar^{-1}\widetilde{H}_0 t} |0\rangle, \qquad (5)$$

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

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

To get function $N_k(\epsilon)$ one calculates the GF $G_{kk'}(\epsilon)$ (see details in Refs. [1,2,9]:

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

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

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

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:

$$D_k(\in) = \in - [\in^{\mathrm{op}} + \Sigma(\in)]_k, \qquad (10)$$

where $(\in^{\mathrm{op}} + \Sigma)_k$ denotes the k-th eigenvalue of the diagonal matrix of the one-particle energies added to matrix of the self-energy part, are the negative V. I. P. 's for a given geometry. One can write [1,5,9]:

$$(V.I.P.)_k = -(\in_k + F_k),$$
$$F_k = \Sigma_{\mathrm{kk}}\left(-(V.I.P.)_k\right) \approx \frac{1}{1 - \partial \Sigma_{\mathrm{kk}}(\in_k)/\partial_\in} \Sigma_{\mathrm{kk}}(\in_k) \qquad (11)$$

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 δQ_S, and new coupling constants:

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

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

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

$$\sum_{kk}^{(2)}(\in) = \sum_{\substack{i,j \\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s\notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} \qquad (13)$$

and the coupling constant g_l, are as [1,3]:

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

The pole strength of the corresponding GF:

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

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

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

It is important to underline that computing the latter parameters by the standard methods requires serious resources. But there is more effective and quite precise approach to this problem. It is connected with using quasiparticle Fermi-liquid theory of the DFT in versions [1,5-7,9]. Especially this approach is effective in computing he vertical I.P. (V.I.P.s), phoelectron spectra (the coupling constants of vibrational structure). The master equations can be obtained on the basis of variational principle, if one starts from a Lagrangian of a molecule L_q [5,7]. It should be defined as a functional of quasiparticle densities:

$$v_0(r) = \sum_\lambda n_\lambda |\Phi_\lambda(r)|^2, \qquad (16)$$

$$v_1(r) = \sum_\lambda n_\lambda |\nabla\Phi_\lambda(r)|^2, \qquad (17)$$

$$v_2(r) = \sum_\lambda n_\lambda[\Phi_\lambda^*\Phi_\lambda - \Phi_\lambda^*\Phi_\lambda]. \qquad (18)$$

The densities v_0 and v_1 are similar to the HF electron density and kinetical energy density correspondingly; the density v_2 has no an analog in the HF or DFT theory and appears as result of account for the energy dependence of the mass operator Σ. A Lagrangian L_q can be written as a sum of a free Lagrangian and Lagrangian of interaction: $L_q = L_q^0 + L_q^{int}$, where 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:

$$L_q^{\mathrm{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2}\int \beta_{ik}F(r_1,r_2)v_i(r_1)v_k(r_2)dr_1 dr_2 \qquad (19)$$

where F is an effective exchange-correlation interaction potential. The constants β_{ik} are defined in Refs. [1,5,6]. 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} [5-7]:

$$F_{sp} = \left\{1 - \frac{\partial}{\partial \in}\sum_{kk}[-(V.I.P.)_k]\right\} \qquad (20)$$

The multiplier $[1-\Sigma_2]$ is easily calculated if the Gunnarsson-Lundqvist-like correlation potential is used as V_{XC} and Σ_2 is determined as fol-

lows:

$$\sum(r) = 0.254\rho(r)[0.328\rho^{-2/3}(r) +$$

(21)

$$+ 0.204\rho^{-2/3}(r)/\{1 + 18.376\rho^{1/3}(r)\}]$$

The new element is linked with using the DFT correlation Gunnarsson-Lundqvist as well as the Lee-Yang-Parrr functionals etc. (c.g.[12-16]). For all calculations it has been used the PC code Supermolecule (version 93).

4. Results and conclusions

As an illustration, Table 1 shows the experimental values of VIP (a), single-particle HF energies (b), the value of VIP calculated on the basis of the Koopmans theorem (KT) plus the reorganization correction (EKT; c), VIP calculated by the usual and extended GF method (d,f,g), our data within the combined GF-DFT theory (h). For comparison, the data of the multi-configuration electron propagator (MCEP) method, an extended theory using Koopmans' theorem (EKT) are also given (the extended EKT theory uses multi-configurational self-consistent wave functions with different sets of electron orbital basis functions (from res. [1-3,7,8,13,14]).

Table 1. Theoretical and experimental VIPs (eV) for the nitrogen molecule: experiment (a), HF single-particle energies (b), VIP values based on Koopmans' theorem (KT) plus reorganization correction (EKT; c), VIP calculated by the conventional and extended method GF (d,f,g), data from the multi-configuration electron propagator (MCEP;e) method, our data from the combined GF-DFT theory (h).

Orbital	Exp (a)	KT $-\in_k^b$ (b)	EKT $-\in_k^b$ (c)	GF $-\in_k^b$ (d)
$3\sigma_g$	15.6	17.24	16.37; 16.13 16.84; 15.66	15.31
$1\pi_u$	16.98	16.73	16.73	16.80
$2\sigma_u$	18.78	21.13	21.13	19.01
Orbital	MCEP $-\in_k^b$ (e)	GF+ Reorg (f)	GF-All (g)	Our Data (h)
$3\sigma_g$	15.52	16.0	15.50	15.58
$1\pi_u$	17.24	15.7	16.83	16.97
$2\sigma_u$	18.56	19.9	18.59	18.77

In table 2. given data for the bond constants g (in eV) for the N_2 molecule in different approximations: g^0 – the value of the constant g in the HF approximation without taking into account corrections for correlation and reorganization; g^R is the value of the constant g, taking into account only the correction for the effect of reorganization; $g^{R+C(a)}$ and $g^{R+C(b)}$ - are values of the constant g, taking into account corrections for correlation and reorganization, obtained within the framework of the Sederbaum-Domsky DFT method (a) and our QP-DFT (b).

Table 2 Bond constant g (in eV) in different approximations for the N_2 molecule (see text)

Orbital	g^0	g^R
$3\sigma_g$	-0.095	-0.074
$1\pi_u$	-0.344	-0.334
$2\sigma_u$	+0.268	+0.267
Orbital	$g^{R+C\,(a)}$	$g^{R+C\,(b)}$
$3\sigma_g$	-0.0965	-0.0964
$1\pi_u$	-0.337	-0.3302
$2\sigma_u$	+0.177	+0.1635

The results listed in the tables show slightly better agreement between data of the presented approach and experiment than the results of calculations in other versions of the DV method.

It is obvious that a carrying out more perfect than the existing methods to computing spectral molecular characteristics of molecular systems should include more careful accounting for correlation effects,. Developed one-quasiparticle representation used here can be taken as the zeroth approximation in one of the sophisticated versions of the many-body PT such as , for example, the Möller-Plesset PT etc.

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Keywords: optimized one-quasiparticle approximation, Green's function, density functional, diatomic molecules, spectral characteristics

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МЕТОД ФУНКЦІОНАЛУ ГУСТИНИ ТА ФУНКЦІЙ ГРІНА ДЛЯ ОБЧИСЛЕННЯ СПЕКТРАЛЬНИХ ПАРАМЕТРІВ ДВОХАТОМНИХ МОЛЕКУЛ

Резюме. Викладено новий ефективний метод обчислення енергетичних та спектральних параметрів двоатомних молекул, що базується на гібридній теорії квазічастинкового функціонала густини і теорії функцій Гріна. Як ілюстрація наведені дані обчислення вертикальних потенціалів іонізації і констант зв'язку (коливальної структури) фотоелектронних спектрів ряду двохатомних молекул, зокрема, N_2. Проведено докладне

порівняння деяких отриманих даних з даними стандартних теорій типу Хартрі-Фока, методу багатоконфігураційного електронного пропагатору, розширеною теорією на основі теореми Koopmans' з використанням багатоконфігураційних самоузгоджених хвильових функцій з різними наборами базисних функцій. Показано, що послідовне максимально коректне врахування обмінно-кореляційних ефектів, ефектів реорганізації в рамках комбінованої теорії призводить до досить істотного поліпшення згоди теоретичних та експериментальних даних як по потенціалам іонізації, так й фотоелектронним спектрам взагалі.

Ключові слова: оптимізоване одноквазічастинкове наближення**,** функція Гріна, функціонал густини, двоатомні молекули, спектральні характеристики