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PHOTOELECTRON SPECTROSCOPY OF DIATOMIC MOLECULES: OPTIMIZED GREEN'S FUNCTIONS AND DENSITY FUNCTIONAL APPROACH

We present the optimized version of the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach to quantitative treating the diatomic photoelectron spectra. The Fermi-liquid quasiparticle version of the density functional theory is 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 the calculation and increasing an accuracy of theoretical prediction.

Introduction

In this paper we present the optimized version of the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach to quantitative treating the diatomic photoelectron spectra..

The approach is based on the Green's function method (Cederbaum-Domske version) [11,12], Fermi-liquid DFT formalism [1-8] and use of the novel effective density functionals (see also [13-16]). 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 method becomes a powerful tool in interpreting the vibrational structure of photoelectron spectra for different molecular systems.

As usually (see details in refs. [1-12]), the quantity which contains the information about the ionization potentials (I.P.) and molecular vibrational structure due to quick ionization is the density of occupied states:

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

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

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

As usually, introducing a field operator $\sum$ with the Hartree-Fock (HF) one–particle functions ϕ_i ($\in$ 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 [2,11]:

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

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

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

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

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

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

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

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

$$[\delta v_1 a_i^t a_j^t a_k + \delta v_2 a_l a_k a_i^t a_j^t + 2\delta v_3 a_j^t a_k a_l a_i^t]$$

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 and or and are unoccupied, v_2 that at most one of the orbitals is unoccupied, and v_3 that and or and are unoccupied. The are the HF frequencies; , 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. [1,2,11,12]. The usual way is to define the HF-single-particle component of the Hamiltonian (4) is as in Refs. [11,12]. Correspondingly in the one-particle picture the density of occupied states is given by

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

$$\widetilde{H}_0 = \sum_{s=1}^{M} \hbar\omega_s b_s^t b_s + \sum_{s=1}^{M} g_s^k (b_s + b_s^t) + \qquad (6)$$

$$+ \sum_{s,s'=1}^{M} \gamma_{ss'}^k (b_s + b_s^t)(b_{s'} + b_{s'}^t)$$

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

In a diagrammatic method to get function ω one should calculate the GF $_k$ ω first [1,2,11,12]:

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

and the function ω can be found from the relation

$$\pi N_k(\omega) = a\,\mathrm{Im}\ G_{kk}\ \omega - i\eta\ ,\ a = -sign\,\omega\ . \qquad (9)$$

Choosing the unperturbed Hamiltonian to be $\sum$ ω one could define the GF as follows:

$$G_{kk'}^{0}(t) = \pm\delta_{kk'} i\exp\left[-i\omega^{-1}(\varepsilon_k \mp \Delta\varepsilon)t\right]\cdot$$
$$\cdot\sum_n \left|\langle\hat{n}_k|U_k|0\rangle\right|^2 \exp(\pm i\omega_k \cdot \hat{\omega}_k t) \qquad , (10)$$

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

$$D_k(\in) = \in - [\in^0 + \Sigma(\in)]_k, \qquad (11)$$

where $(\in^0 + \Sigma)_k$ 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 [2,11,12]:

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

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

. (12)

Expanding the ionic energy 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:

$$g_1 = \pm(1/\sqrt{2})[\partial(\in_k + F_k)/\partial Q_l]_0 \qquad (13)$$

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

The coupling constants and , are calculated by the well-known perturbation expansion of the self-energy part. In second order one obtains:

$$\sum\nolimits_{k}^{(2)}(\in) = \sum_{\substack{i,j \\ s\notin F}} \frac{\left(V_{ksij} - V_{ksji}\right)V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s\notin F}} \frac{\left(V_{ksij} - V_{ksji}\right)V_{ksij}}{\in + \in_s - \in_i - \in_j} \quad (14)$$

and the coupling constant g_l, are written as [17]:

$$g_l \approx \pm\frac{1}{\sqrt{2}}\frac{\partial \in_k}{\partial Q_l}\frac{1 + q_k\left(\partial/\partial \in\right)\sum_{k}\left[-\left(V.I.P.\right)_k\right]}{1 - \left(\partial/\partial \in\right)\sum_{k}\left[-\left(V.I.P.\right)_k\right]} \quad (15)$$

The pole strength of the corresponding GF:

$$\rho_k = \left\{1 - \frac{\partial}{\partial \in}\sum_{k}\left[-(V.I.P)_{k}\right]\right\}^{-1}; 1 \geq \rho_k \geq 0,$$
$$g_l \approx g_l^0\left[\rho_k + q_k\left(\rho_k - 1\right)\right],$$
$$\pm \quad \partial \in \quad \partial \quad (16)$$

Below we give another the definition of the pole strength corresponding to V. I. P.'s.

3. Fermi-liquid quasiparticle density functional theory

The quasiparticle Fermi-liquid version of the DFT [1-3,8,17] 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:

$$\sum$$
$$\sum \quad \nabla \quad (17)$$
$$_2(r) \quad \sum n\,[\ ^{*} \qquad ^{*}\ ]$$

The densities ν_0 and ν_1 are similar to the HF electron density and kinetical energy density correspondingly; the density ν_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), however, it takes into account for the energy dependence of a mass operator Σ :

$$L_q^{\text{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2}\int \beta_k F(r_1, r_2)\nu_i(r_1)\nu_k(r_2)\mathbf{d}_1\mathbf{d}_2 \quad (18)$$

where F is an effective potential of the exchange-correlation interaction. The constants β_{ik} are defined in Ref. [8,17]. The single used constant β_{02} can be calculated by analytical way, but it is very useful to remember its connection with a spectroscopic factor F_{sp} of the system [18]:

$$F_{sp} = \left\{1 - \frac{\partial}{\partial \in}\sum_{k}\left[-(V.I.P)_{k}\right]\right\} \quad (19)$$

The terms $\partial\sum\partial$ and $\sum$ is directly linked [2,17]. In the terms of the Green function method expression (7) is in fact corresponding to the pole strength of the Green's function [2]. The new element of an approach is connected with using the DFT correlation functional of the Gunnarsson-Lundqvist, Lee-Yang-Parr (look details in ref. [13-16]).

3. Results and conclusions

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]. 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. As an object of studying we choose the diatomic molecule of N_2 for application of the combined Green's function method and quasiparticle DFT approach. The nitrogen molecule has been naturally discussed in many papers. The valence V. I. P. of N_2 have been calculated [1,13,14,24] 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. It should be reminded that the N_2 molecule is the classical example where the known Koopmans' theorem (KT) even fails in reproducing the sequence of the V. I. P. 's in the PE spectrum. From the HF calculation of Cade *et al.*[24] one finds that including reorganization the V. I. P. 's assigned by and improve while for 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. In Table 1 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 functions and DFT approach (e), the similar our results (f).

Table 1.

The experimental and calculated V. I. P. (in eV) of N_2 (R_k is the contribution of reorganization (see text)

	Exp	KT $-\epsilon_k^b$	EKT $-\epsilon_k^b$	GF $-\epsilon_k^b$	MCEP $-\epsilon_k^b$
$3\sigma_g$	15.6	17.24	16.37 16.13 16.84 15.66	15.31	15.52
$1\pi_u$	16.98	16.73	16.73	16.80	17.24
$2\sigma_u$	18.78	21.13	21.13	19.01	18.56
	Exp	GF+ Reorg.	GF- All corr	GF- DFT	This work
$3\sigma_g$	15.6	16.0	15.50	15.52	15.58
$1\pi_u$	16.98	15.7	16.83	16.85	16.93
$2\sigma_u$	18.78	19.9	18.59	18.63	18.71

Besides, the comparisons are made in Table 1 with the multiconfigurational electron propagator method (MCEP) and extended KT (EKT) theory (the extended KT has been implemented using multiconfigurational self-consistent field wave functions within different basis sets (I-IV) [52], calculated with the GAMESS, HONDO, and SIRIUS programs. The EKT ionization energies for the 3 and 1 are comparable to the MCEP values. Note that our data are in physically reasonable agreement with the best theretixl values and experimental data. But the most important point of all consideration is connected the principal possibility to reproduce diatomic spectra by applying a one-particle theory with accounting for the correlation and reorganization effects. The combined DFT-GF theoretical approach can be prospectively used for quantitative treating photoelectron spectra of more complicated diatomic molecules.

References

1. Glushkov A.V., New approach to theoretical definition of ionization potentials for molecules on the basis of Green's function method// Journ.of Phys.Chem.-1992.-Vol.66.-P.2671-2677.
2. Glushkov A.V., Relativistic quantum theory. Quantum mechanics of atomic systems.-Odessa: Astroprint, 2008.-700P.
3. Glushkov A.V., The Green's functions and density functional approach to vibrational structure in the photoelectron spectra of molecules: Review of method// Photoelectronics.-2014.-Vol.23.-P.54-72.
4. Glushkov A.V., Lepikh Ya.I., Fedchuk A.P., Loboda A.V., The Green's functions and density functional approach to vibrational structure in the photoelectron spectra of molecules//Photoelectronics.-2009.-N18.-P.119-127.
5. Svinarenko A.A., Fedchuk A.P., Glushkov A.V.,Lepikh Ya.I., Loboda A.V., Lopatkin Yu.M., The Green's functions and density functional approach to vibrational structure in the photoelectron spectra of carbon oxide molecule//Photoelectronics.-2010.-N19.-P.115-120.
6. Glushkov A.V., Fedchuk A.P., Kon-

dratenko P.A., Lepikh Ya.I., Lopatkin Yu.M., Svinarenko A.A., The Green's functions and density functional approach to vibrational structure in the photoelectron spectra: Molecules of CH, HF//Photoelectronics.-2011.-Vol.20.-P.58-62.
7. Glushkov A.., Koltzova N., Effective account of polarization effects in calculation of oscillator strengths and energies for atoms and molecules by method of equations of motion// Opt. Spectr. -1994.- Vol. 76,№6.-P.885-890.
8. Glushkov A.V., Quasiparticle approach in the density functional theory under finte temperatures and dynamics of effective Bose -condensate // Ukr. Phys. Journ..- 1993.-Vol. 38, №8.-P.152-157.
9. Ponomarenko E.L., Kuznetsova A.A., Dubrovskaya Yu.V., Bakunina (Mischenko) E.V., Energy and spectroscopic parameters of diatomics within generalized equation of motion method// Photoelectronics.-2016.-Vol.25.-P.114-118.
10. Mischenko E.V., An effective account of correlation in calculation of excited states energies for molecules by equation of motion method: O_3//Photoelectronics.-2007.-N16.-P.123-125.
11. Köppel H., Domcke W., Cederbaum L.S., Green's function method in quantum chemistry// Adv. Chem. Phys.-1984.-Vol.57.-P.59-132.
12. Cederbaum L.S., Domcke W., On vibrational structure of photoelectron spectra by the Green's functions method// J.Chem. Phys.-1984.-Vol.60.-P.2878-2896.
13. Zangwill A.,Soven P.J. Density-functional approach to local field effects in finite systems. Photo-absorption in rare gases // Phys.Rev.A.-1980.-Vol.21,N5-P.1561-1572.
14. Kobayashi K., Kurita N., Kumahora H., Kuzatami T. Bond-energy calculations of Cu , Ag, CuAg with the generalized gradient approximation// Phys. Rev.A.-1991.-Vol.43.-P.5810-5813.
15. Lagowscki J.B., Vosko S.H. Analysis of local and gradient- correction correlation energy functionals using electron removal energies// J. Phys.B: At. Mol. Opt. Phys.-1988.-Vol.21,N1-P.203-208.
16. Guo Y., Whitehead M.A. Effect of the correlation correction on the ionization potential and electron affinity in atoms// Phys.Rev.A-1989.-Vol.39,N1.-P.28-34.
17. Glushkov A.V., An universal quasiparticle energy functional in a density functional theory for relativistic atom// Optics and Spectr.-1989.-Vol.66,N1-P.31-36.
18. Glushkov A.V., Relativistic and correlation effects in spectra of atomic systems.-Odessa: Astroprint.-2006.-400P.
19. Glushkov A.V., Atom in electromagnetic field.-Kiev: KNT, 2005.-450P.
20. Khetselius O.Yu., Hyperfine structure of atomic spectra.-Odessa: Astroprint, 2008.-210P.
21. Glushkov A.V., Khetselius O.Y., Malinovskaya S.V., Spectroscopy of cooperative laser-electron nuclear effects in multiatomic molecules// Molec. Phys.-2008. -Vol.106.-N9-10.-P.1257-1260.
22. Glushkov A.V., Khetselius O.Y., Malinovskaya S.V., New laser-electron nuclear effects in the nuclear γ transition spectra in atomic and molecular systems// Frontiers in Quantum Systems in Chemistry and Physics. Series: Progress in Theoretical Chemistry and Physics , Eds. S.Wilson, P.J.Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch (Springer).-2008.-Vol.18.-525-541.
23. Glushkov A.V., Khetselius O.Yu., Svinarenko A.A., Prepelitsa G.P. , Shakhman A., Spectroscopy of co-

operative laser-electron nuclear processes in diatomic and multiatomic molecules//Spectral Lines Shape (AIP, USA).-2010.-Vol.16.-P.269-273.
24. Glushkov A.V., Kondratenko P.A., Buyadzhi V., Kvasikova A.S., Shakhman A., Sakun T., Spectroscopy of cooperative laser electron-γ-nuclear processes in polyatomic molecules// Journal of Physics: C Series (IOP, London, UK).-2014.-Vol.548.-P. 012025 (5p.).
25. Glushkov A.V., Kondratenko P.A., Lopatkin Yu., Buyadzhi V., Kvasikova A., Spectroscopy of cooperative laser electron- γ -nuclear processes in diatomics and multiatomic molecules // Photoelectronics.-2014.-Vol.23.-P.142-146.
26. Khetselius O.Yu., Optimized perturbation theory to calculating the hyperfine line shift and broadening for heavy atoms in the buffer gas// Frontiers in Quantum Methods and Applications in Chemistry and Physics. Ser.: Progress in Theor. Chem. and Phys., Eds. M.Nascimento, J.Maruani, E.Brändas, G.Delgado-Barrio (Springer).-2015-Vol.29.-P.54-76.
27. Khetselius O.Yu., Relativistic energy approach to cooperative electron-γ-nuclear processes: NEET Effect// Quantum Systems in Chemistry and Physics: Progress in Methods and Applications. Ser.: Progress in Theor. Chem. and Phys., Eds. K.Nishikawa, J. Maruani, E.Brandas, G. Delgado-Barrio, P.Piecuch (Springer).-2012-Vol.26.-P.217-229.
28. Buyadzhi V.V., Glushkov A.V., Lovett L., Spectroscopy of atoms and nuclei in a strong laser field: AC Stark effect and multiphoton resonances// Photoelectronics.-2014.-Vol.23.-P. 38-43.
29. Khetselius O., Spectroscopy of cooperative electron-gamma-nuclear processes in heavy atoms: NEET effect// J. Phys.: Conf. Ser.-2012.- Vol.397.-P.012012
30. Glushkov A.V., Khetselius O.Yu., Loboda A.V., Svinarenko A.A., QED approach to atoms in a laser field: Multi-photon resonances and above threshold ionization// Frontiers in Quantum Systems in Chemistry and Physics, Ser.: Progress in Theoretical Chemistry and Physics; Eds. S.Wilson, P.J.Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch (Springer), 2008.-Vol.18.-P.541-558.
31. Glushkov A.V., Khetselius O.Yu., Svinarenko A.A., Prepelitsa G.P., Energy approach to atoms in a laser field and quantum dynamics with laser pulses of different shape//In: Coherence and Ultrashort Pulse Laser Emission, Ed. by Dr. F. Duarte (InTech).-2010.-P.159-186.
32. Glushkov A.V., Khetselius O., Svinarenko A, Relativistic theory of cooperative muon-g gamma-nuclear processes: Negative muon capture and metastable nucleus discharge// Advances in the Theory of Quantum Systems in Chemistry and Physics. Ser.: Progress in Theor. Chem. and Phys., Eds. P.Hoggan, E.Brandas, J.Maruani, G. Delgado-Barrio, P.Piecuch (Springer).-2012.-Vol.22.-P.51-68.
33. Glushkov A.V., Khetselius O.Yu., Prepelitsa G., Svinarenko A.A., Geometry of Chaos: Theoretical basis's of a consistent combined approach to treating chaotic dynamical systems and their parameters determination //Proc. of International Geometry Center".-2013.-Vol.6, N1.-P.43-48.
34. Malinovskaya S.V., Glushkov A.V., Dubrovskaya Yu.V., Vitavetskaya L.A., Quantum calculation of cooperative muon-nuclear processes: discharge of metastable nuclei during negative muon capture// Recent Advances in the Theory of Chemical and Physical Systems (Springer).-2006.-

Vol.15.-P.301-307.
35. Malinovskaya S.V., Glushkov A.V., Khetselius O.Yu., Lopatkin Yu., Loboda A., Svinarenko A., Nikola L., Perelygina T., Generalized energy approach to calculating electron collision cross-sections for multicharged ions in a plasma: Debye shielding model// Int. Journ. Quant. Chem.-2011.-Vol.111,N2.-P.288-296.
36. Malinovskaya S.V., Glushkov A.V., Khetselius O.Yu., Svinarenko A.A., Mischenko E.V., Florko T.A., Optimized perturbation theory scheme for calculating the interatomic potentials and hyperfine lines shift for heavy atoms in the buffer inert gas//Int. Journ. Quant.Chem.-2009.-Vol.109,N14.-P.3325-3329.
37. Glushkov A.V., Khetselius O.Yu., Svinarenko A., Prepelitsa G., Mischenko E., The Green's functions and density functional approach to vibrational structure in the photoelectron spectra for molecules// AIP Conf. Proceedings.-2010.-Vol.1290.-P. 263-268.
38. Khetselius O.Yu., Florko T.A., Svinarenko A.A., Tkach T.B., Radiative and collisional spectroscopy of hyperfine lines of the Li-like heavy ions and Tl atom in an atmosphere of inert gas//Phys.Scripta.-2013.-Vol.T153-P.014037.
39. Khetselius O.Yu., Hyperfine structure of radium// Photoelectronics.-2005.-N14.-P.83-85.
40. Glushkov A.V, Malinovskaya S.,Co-operative laser nuclear processes: border lines effects// In: New projects and new lines of research in nuclear physics. Eds. G.Fazio, F.Hanappe, Singapore: World Scientific.-2003.-P.242-250.
41. Glushkov A.V., Lovett L., Khetselius O., Gurnitskaya E., Dubrovskaya Yu., Loboda A., Generalized multiconfiguration model of decay of multipole giant resonances applied to analysis of reaction (m-n) on the nucleus ^{40}Ca// Internat. Journ. Modern Physics A.-2009.- Vol. 24, N.2-3.-P.611-615.
42. Glushkov A., Malinovskaya S., Sukharev D., Khetselius O.Yu., Loboda A., Lovett L., Green's function method in quantum chemistry: New numerical algorithm for the Dirac equation with complex energy and Fermi-model nuclear potential//Int.J. Quant. Chem.-2009.- Vol. 109.-N8.-P.1717-1727.
43. Glushkov A.V., Malinovskaya S.V, Gurnitskaya E.P., Khetselius O.Yu., Dubrovskaya Yu.V., Consistent quantum theory of the recoil induced excitation and ionization in atoms during capture of neutron// Journal of Physics: Conf. Series (IOP).-2006.-Vol.35.-P.425-430.
44. Glushkov A V, Khetselius O Yu, Svinarenko A A and Buyadzhi V V, Spectroscopy of autoionization states of heavy atoms and multiply charged ions (Odessa: TEC), 2015
45. Khetselius O.Yu., Turin A.V., Sukharev D.E., Florko T.A., Estimating of X-ray spectra for kaonic atoms as tool for sensing the nuclear structure// Sensor Electr. and Microsyst. Techn.-2009.-N1.-P.30-35.
46. Glushkov A.V., Effective quasi-particle valence hamiltonian of molecules in the comprehensive semi-empirical theory// Sov. J. Struct. Chem.-1988.-Vol.29,N4.-P.3-9.
47. Khetselius O.Yu., Quantum Geometry: New approach to quantization of the quasistationary states of Dirac equation for super heavy ion and calculating hyper fine structure parameters// Proc. Int.Geometry Center.-2012.-Vol.5,№ 3-4.-P.39-45.
48. Glushkov A.V., Khetselius O.Yu., Svinarenko A.A., Theoretical spectroscopy of autoionization resonances in spectra of lanthanide atoms//

Physica Scripta.-2013.-Vol.T153.-P.014029.
49. Gedasimov V N, Zelenkov A G, Kulakov V M et al 1984 *JETP.* **86** 1169; Soldatov A A 1983 Preprint of I.V.Kurchatov Institute for Atomic Energy IAE-3916, Moscow
50. Glushkov A.V., Operator Perturbation Theory for Atomic Systems in a Strong DC Electric Field//Advances in Quantum Methods and Applications in Chemistry, Physics, and Biology. Series: Frontiers in Theoretical Physics and Chemistry, Eds. M.Hotokka, J.Maruani, E. Brändas, G.Delgado-Barrio (Springer).-2013.-Vol. 27.-P.161-177.
51. Glushkov A.V., Kondratenko P.A., Lepikh Ya., Fedchuk A.P., Svinarenko A.A., Lovett L., Electrodynamical and quantum - chemical approaches to modelling the electrochemical and catalytic processes on metals, metal alloys and semiconductors// Int. J. Quantum Chem.-2009.-Vol.109, N14.-P.3473-3481.
52. Robert C. Morrison R., Liu G., Extended Koopmans' Theorem: Approximate Ionization Energies from MCSCF Wave Functions// J. Comput. Chem.-1992.-Vol. 13.-P.1004-1010.

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

Summary

We present the optimized version of the hybrid combined density functional theory (DFT) and the Green's-functions (GF) approach to quantitative treating the diatomic photoelectron spectra. The Fermi-liquid quasiparticle version of the density functional theory is 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 the calculation and increasing an accuracy of theoretical prediction.

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

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ОБОБЩЕННЫЙ МЕТОД ФУНКЦИЙ ГРИНА И ФУНКЦИОНАЛА ПЛОТНОСТИ В ОПРЕДЕЛЕНИИ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ ФОТОЭЛЕКТРОННОГО СПЕКТРА ДВУХАТОМНЫХ МОЛЕКУЛ

Резюме

Мы представляем оптимизированную версию гибридной комбинированной теории функционала плотности (DFT) и метода функций Грина (GF) для количественного описания фотоэлектронных спектров двухатомных молекул. Используется модель ферми-жидкостная квазичастичная версия теории функционала плотности. Плотность состояний, которые описывают колебательную структуру в фотоэлектронных спектрах, определяется с использованием комбинированного DFT-GF подхода и физически разумно аппроксимируется с использованием только первого порядка констант связи в одноквазичастичном приближении. Использование комбинированного DFT-GF подхода приводит к значительному упрощению молекулярных расчетов и увеличению точности теоретического предсказания.

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

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УДОСКОНАЛЕНИЙ МЕТОД ФУНКЦІЙ ГРІНА І ФУНКЦІОНАЛУ ГУСТИНИ У ВИЗНАЧЕННІ ВІБРАЦІЙНОЇ СТРУКТУРИ ФОТОЕЛЕКТРОННОГО СПЕКТРУ ДВОАТОМНИХ МОЛЕКУЛ

Резюме

Ми представляємо оптимізовану версію гібридної комбінованої теорії функціоналу густини (DFT) і методу функцій Грина (ГФ) для кількісного опису фотоелектронних спектрів двохатомних молекул. Використовується фермі-рідинна квазічастична версія теорії функціоналу густини. Густина стану, яка описує коливальну структуру в фотоелектронних спектрах, визначається з використанням комбінованого DFT-GF підходу та фізично розумно апроксимується за допомогою тільки першого порядку констант зв'язку в одноквазічастинковому наближенні. Використання комбинированного DFT-GF подхода призводить до значного спрощення молекулярних обчислень та збільшення точності теоретичного прогнозування.

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