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ENERGY AND SPECTROSCOPIC PARAMETERS OF DIATOMICS WITHIN GENERALIZED EQUATION OF MOTION METHOD

The spectral data on energies of transitions in spectrum of the nitrogen diatomics e are presented on the basis of calculation by modified motion equations method (MEM) with effective account for important correlation effects within a density functional approach. It differs from the standard version of the MEM by method by effective accounting for interelectron correlation effects, namely, effects of the "two holes- two particles". As a result an inaccuracy of calculation of the molecular excited states energies decreases significantly in comparison with the standard 1p-1h MEM approximation, namely, from 1.5-2 eV to decimal parts of eV, if you take into account the 2p-2h effects.

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 [1]. Information about excitation energies, probabilities and oscillator strengths of electron transitions in molecules is very important for a whole number of applications including different fields of a photo-chemistry and photophysics. Different calculation methods, namely, ab initio method of multi-configuration interaction (MCI), perturbation theory with Hartree-Fock zeroth approximation (Möller-Plesset theory), density functional theory (DF) etc [1] are used in calculations of atoms and molecules. As alternative in this situation one may consider method of equations of motion (MEM), which has been initially carried out by McKoy and co-workers with account for correlation effects within random phase approximation (RPA) (c.f.[2,3]). In series of papers [4-7] new approach in the MEM, based on account of correlation effects within DF approximation and essentially improving the standard version of the MEM, has been developed. Such an approach allows direct calculating amplitudes of different quantum processes, including absorption and emission of photons etc., and avoiding problems, connected with calculation of the wave functions and entire energies of molecules. Though it does not provide exact results, as for example, known limited variants of variation solving problem, however, it is sufficiently effective in calculations of the excitation energies and oscillator strengths of the electron transitions. In this paper new advanced method, which generalizes the MEM one is presented and applied to determination calculation of the transition energies and oscillator strengths for the nitrogen molecule. It differs from the standard version of the MEM by method to effective accounting for interelectron correlation effects, namely, effects of the "two holes- two particles" (2h-2p) polarization interaction). As it is shown, for example, in ref. [4,5], on order to reach an acceptable accuracy of calculation one may use sufficiently limited (on volume) basis's of orbitals. However, an account of such important correlation effects (effects, connected with 2*p*-2*h* interactions, a pressure of continuum, energy dependence of the self-consistent field potential, etc.) is obligatorily needed. It is well known that an account of majority of these effects based on standard methodic (for example, within perturbation theory) results in significant complication of calculation procedure (c.f. [1-4]).

According to ref. [2,], operator Q_λ^+, which generates an excited state $|\lambda\rangle$ of the atom from the ground state $|0\rangle$, i.e. $|\lambda\rangle = Q_\lambda^+ |0\rangle$, is an exact solution of equation of motion:

$$\langle 0 \| \left[\delta Q_\lambda , H, Q_\lambda^+ \right] \| 0 \rangle = \omega_\lambda \left[\delta Q_\lambda , Q_\lambda^+ \right], \qquad (1)$$

Here w_l is the transition frequency, amplitudes Q_λ^+ are elements of matrix of the transition $|0\rangle$ ® $|\lambda\rangle$. Equation (1) can be reduced to matrix equation for amplitudes $\{Y_{mg}\}$ и $\{Z_{mg}\}$ with account for the 1p-1h excitations as:

$$\begin{vmatrix} A & B \\ -B^* & -A^* \end{vmatrix} \begin{Vmatrix} Y(\lambda) \\ Z(\lambda) \end{Vmatrix} = \omega_\lambda \begin{vmatrix} D & 0 \\ 0 & D \end{vmatrix} \begin{Vmatrix} Y(\lambda) \\ Z(\lambda) \end{Vmatrix}, \quad (2)$$

the matrix elements A, B, D are as follows:

$$\begin{aligned} A_{m\gamma n\delta} &= \left\langle \left\| \left[C_{m\gamma} , H, C_{n\delta}^+ \right] \right\| \right\rangle, \\ B_{m\gamma n\delta} &= \left\langle \left\| \left[C_{m\gamma} , H, C_{n\delta}^+ \right] \right\| \right\rangle, \\ D_{m\gamma n\delta} &= \left\langle \left\| \left[C_{m\gamma} , H, C_{n\delta}^+ \right] \right\| \right\rangle, \end{aligned} \qquad (3)$$

Here C^+ is the particle-hole creation operator (C – destroying), indexes m, n denote the particles states; indexes d, g – the holes states; H is a Hamiltonian of quantum system in the representation of second quantization. The wave function of the ground state can be chosen in the following form:

$$|0\rangle \cong N_0 (1+U) |HF\rangle, \qquad (4)$$

where $U = (1/2) \sum C_{m\gamma n\delta} C_{m\gamma}^+ C_{n\delta}^+, |HF\rangle$ is the Hartree-Fock function. With account for equation (4) the matrix elements A, B, D have the following form:

$$\begin{aligned} A_{m\gamma n\delta} &= A^0_{m\gamma n\delta} + \delta_{\gamma\delta} \left[T_{mn} - (1/2)(\varepsilon_m + \varepsilon_n - 2\varepsilon_\gamma) \rho^{(2)}_{mn} \right] \\ &- \delta_{mn} \left[T_{\gamma\delta} - (1/2)(\varepsilon_m - \varepsilon_\gamma - \varepsilon_\delta) \rho^{(2)}_{\gamma\delta} \right], \\ B_{m\gamma n\delta} &= B^0_{m\gamma n\delta} + (-1)^\lambda S_{m\gamma n\delta}, \\ D_{m\gamma n\delta} &= \delta_{mn} \delta_{\gamma\delta} + \delta_{mn} \rho^{(2)}_{\gamma\delta} - \delta_{\gamma\delta} \rho^{(2)}_{\gamma\delta}. \end{aligned} \qquad (5)$$

The matrices A^0, B^0 etc are in details described in ref. [15]. Variables e in eq. (5) define the Hartree-Fock orbital energies; $\rho^{(2)}_{mn}$ and $\rho^{(2)}_{\gamma\delta}$ are the corrections to matrix of density of the second order and dependent upon correlation coefficients. If the corrected coefficients are omitted, then matrix elements will be reduced to the corresponding matrix elements of the RPA [2]. In this approximation, the equations of motion for definition of the 1*p*-1*h*-amplitudes $\{Y\}$, $\{Z\}$ and corresponding excitation energies w can be solved by standard methods of linear algebra. Acceptable accuracy of calculation is reached even using the limited basis's of orbitals due to the correct accounting for most important PI effects, connected with excitations of the 2p-2h type. From physical point of view, its inclusion is corresponding to an account for self-consistent reconstruction of the holes orbitals in a process of the virtual excitations in the ground configuration. An account of the 2*p*-2*h*-components in Q_λ^+ is equivalent to renor-malization of matrices in Eq.(3). It leads to dependence on the frequency w and reduces to appearance of the weight multiplier in the matrix elements [14- 18]:

$$a(r) = \left[1 - \Sigma_2(r) \right]^{-1}. \qquad (6)$$

In approximation of the quasiparticle DF a variable S expresses through the corresponding correlation functional [13]. In the simplified form of applying out methodic a variable $a(r)$ can be exchanged by (0) without essential loss of accuracy and according to well known procedure in theory of atomic photo-effect, which is based on the RPA with exchange (c.f.[11]). Indeed, the parameter a is corresponding to the known in spectroscopy one, which is a spectroscopic factor $F_{\gamma\delta}$. Its standard definition for atomic or molecular system (it is usually defined from the ionization cross-sections) [6]:

$$F_{\gamma\delta} = \left\{ 1 - \frac{\partial}{\partial \in} \sum_k \left[-(V.I.P.)_k \right] \right\} \qquad (7)$$

The terms $\partial \sum / \partial \varepsilon$ and $\sum_2$ is directly linked [6]. In the terms of the Green function method expression (7) is in fact corresponding to the pole strength of the Green's function [6]. Calculation

is carried out with using the correlation functional of the Lee-Yang-Parr (LYP) (look details in ref. [8-12]).Note further that amplitudes $\{Y_{mg}\}$ and $\{Z_{mg}\}$ define the moment of transition M_{0l}.

$$M_{0\lambda} = (2)^{1/2} \sum_{m\gamma} \left\{ Y^{*}_{m\gamma}(\lambda) M_{m\gamma} + Z^{*}_{m\gamma}(\lambda) M_{m\gamma} \right\} \qquad (8)$$

and oscillator strength:

$$f_{0\lambda} = (2/3) G \omega_{\lambda} \left| M_{0\lambda} \right|^2 \qquad (9)$$

Here G is the degeneration factor, M_{0l} is the particle-hole matrix element. Besides the procedure of account for the 2p-2h effects, other details of our calculation procedure are fully similar to scheme of the standard MEM approach (c.f.[10,14]). In tables 1 and 2 we present the results of our calculation (d) for the excited states energies and oscillator strengths of some states in N_2.

Table 1.

Excited state energies (eV) for N_2 (see text).

	$B^3\Pi_g$	$a^1\Pi_g$	$A^3\sum_u^+$	$B'^3\sum_g^-$	$W^3\Delta_u$
a	9,6	11,5	8,4	11,3	10,1
b	7,5	8,8	7,8	10,2	9,4
c	8,06	9,66	7,14	9,5	8,59
d	8,12	9,71	7,14	9,6	8,73
E	8,1	9,3	7,8	9,7	8,9
	$a'^1\sum_u^-$	$\omega^1\Delta_u$	$b'^1\sum_u^+$	$c^3\Pi_u$	$b^1\Pi_u$
a	11,3	12,0	16,8	13,3	17,4
b	10,6	11,0	15,0	10,8	14,0
c	9,61	10,2	14,28	11,3	13,92
d	9,74	10,31	14,38	11,39	13,92
E	9,9	10,3	14,4	11,1	12,8

The chosen geometry of the molecule is corresponding to generally accepted one for N_2 [1]. There are also presented the analogous data by McKoy et al in the 1p-1h (a) and 2p2-h (b), Glushkov (c) and experimental data (E) for comparison too. As one can wait for, an account of the 2p-2h effects is very important An inaccuracy of calculation of the transitions energies to low lying excited states in the 1p-1h MEM approximation decreases significantly, namely, from 1.5-2 eV to decimal parts of eV, if you take into account the 2p-2h effects.

Table 2.

Oscillator strengths for some electron transitions in the N_2

State	a	c	d	Exp	
$c'^1\sum_u^+$	0,11	0,10	0,13	0,14 ± 0,04	0,16
$b^1\Pi_u$	0,32	0,26	0,28	<0,3	
$b'^1\sum_u^+$	0,49	0,39	0,41	0,83	0,40

References

1. Ph.Duranrd, J.P.Malriew, Ab initio methods of Quantum Chemistry. Ed. Lawley K.P.,Chichester B.etc., N.-Y.: Academic Press,204.-550p.
2. Rose J., Shibua T., McKoy V., Equations of motion method including renormalization and double excited mixing: Random phase approximation// J.Chem.Phys.-1993.-Vol.58.-P.500-507.
3. Rose J., Shibua T., McKoy V. The equations of motion method in molecular calculations I //J.Chem.Phys.-1993.-Vol.58.- P.74-86.
4. 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.
5. 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.
6. Glushkov A.V., New approach in theoretical determination of molecules ionization potentials on the basis of the Green's functions method // J. of Phys. Chem.-1992.– Vol.66.-P.2671-2677.
7. 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.
8. 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.
9. 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.
10. 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.
11. 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.-1998.-Vol.21,N1-P.203-208.
12. Guo Y., Whitehead M.A. Effect of the correlation correction on the ionization potential and electron affinity in atoms// Phys.Rev.A-1999.-Vol.39,N1.-P.28-34.

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Abstract

The spectral data on energies of transitions in spectrum of the nitrogen diatomics e are presented on the basis of calculation by modified motion equations method (MEM) with effective account for important correlation effects within a density functional approach. It differs from the standard version of the MEM by method by effective accounting for interelectron correlation effects, namely, effects of the “two holes- two particles”. As a result an inaccuracy of calculation of the molecular excited states energies decreases significantly in comparison with the standard 1p-1h MEM approximation, namely, from 1.5-2 eV to decimal parts of eV, if you take into account the 2p-2h effects.

Key words: molecule, inter electron correlation, motion equations method, density functional

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ЭНЕРГЕТИЧЕСКИЕ И СПЕКТРОСКОПИЧЕСКИЕ ПАРАМЕТРЫ ДВУХАТОМНЫХ МОЛЕКУЛ НА ОСНОВЕ РАСЧЕТА ОБОБЩЕННЫМ МЕТОДОМ УРАВНЕНИЙ ДВИЖЕНИЯ

Резюме. На основе расчета обобщенным методом уравнений движения (МУД) с эффективным учетом важнейших корреляционных эффектов в приближении корреляционного функ-

ционала плотности получены энергетические и спектроскопические данные по энергиям возбужденных состояний и силам осцилляторов ряда переходов в молекуле азота. Новая версия отличается от стандартной версии МУД методикой эффективного учета межэлектронного эффектов корреляции, а именно, эффектов типа «двух частицы – две дырки». В результате неточность расчета энергий молекулярных возбужденных состояний значительно уменьшается по сравнению со стандартным 1p-1h МУД приближением, а именно, от 1.5-2 эВ до десятых долей эВ при учета 2p-2h эффектов.

Ключевые слова: молекула, под электронной корреляции, метод уравнений движения, функционал плотности

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ЕНЕРГЕТИЧНІ І СПЕКТРОСКОПІЧНІ ПАРАМЕТРИ ДВОАТОМНИХ МОЛЕКУЛ НА ОСНОВІ РОЗРАХУНКУ УЗАГАЛЬНЕНИМ МЕТОДОМ РІВНЯНЬ РУХУ

Резюме. На основі розрахунку узагальненим методом рівнянь руху (МУР) з ефективним урахуванням найважливіших кореляційних ефектів в наближенні кореляційного функціонала густини отримані енергетичні і спектроскопічні дані по енергіях збуджених станів і силам осциляторів ряду переходів в молекулі азоту. Нова версія відрізняється від стандартної версії МУД методикою ефективного обліку межелектронних ефектів кореляції, а саме, ефектів типу «дві частинки - дві дірки». В результаті неточність розрахунку енергій молекулярних збуджених станів значно зменшується в порівнянні зі стандартним 1p-1h МУД наближенням, а саме, від 1.5-2 еВ до десятих часток еВ при урахування 2p-2h ефектів.

Ключові слова: молекула, міжелектронні кореляції, метод рівнянь руху, функціонал густини