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ON DETERMINATION OF RADIATIVE TRANSITIONS PROBABILITIES IN RELATIVISTIC THEORY OF DIATOMIC MOLECULES: NEW SCHEME

On the basis of new gauge-invariant scheme in the relativistic energy approach combined with the multi-body perturbation theory for diatomic molecules it is formulated a new theoretical scheme for calculating the probabilities of radiative transitions of molecules. It is analysed the possible way to take into account for the inter-electron correlation and correspondingly the non-gauge-invariant contributions in relativistic molecular theory.

1. The experimental and theoretical studying of the radiation transition characteristics of a whole number of many-electron systems such as atoms and diatomic molecules is of a great importance and interest from the point of view of as the quantum electronics and atomic physics as atmosphere, plasma physics and plasma diagnostics science [1-33]). The traditional problem of any theory of the multielectron systems is determination of the radiation transition probabilities (oscillator strengths). Naturally to present time there are many well developed methods in a relativistic theory of atoms and ions and non-relativistic theory of molecular systems [1-16]. The well known multi-configuration Hartree-Fock method (the relativistic effects are often taken into account in the Pauli approximation or Breit Hamiltonian etc) allowed to obtain the useful spectral data on light and not heavy systems. The multi-configuration Dirac-Fock (DF) method is the most reliable version of calculation for systems with a large number of electrons. In these calculations the effects are taken into account practically precisely [1-18]. The calculation program of Desclaux (the Desclaux program, Dirac package) is compiled with proper account of the one- and two-particle relativistic, a finiteness of the nucleus size etc. It should be given special attention to two very general and important computer systems for relativistic calculations of atomic and molecular properties developed in the Oxford group and known as GRASP ("GRASP", "Dirac"; "BERTHA", "QED", "Dirac") (see [1-5] and references there). Besides, the well known density functional theory (DFT), relativistic coupled-cluster approach and model potential approaches in heavy atoms and ions should be mentioned too [1-15].

Nevertheless, as a rule, detailed description of the method for studying role of the relativistic, gauge-invariant contributions, for molecular systems is lacking. Serious problems are connected with correct definition of the high-order correlation corrections etc. The further improvement of this method is connected with using the gauge invariant procedures of generating the electron orbitals basis's and more correct treating the correlation effects [1-5,16-21].

In refs. [5,17-22] it has been performed an analysis of approaches to description of the relativistic many-electron systems with accurate consistent treating the relativistic, exchange-correlation and other, based on the relativistic perturbation theory (PT) formalism.

In the relativistic theory of heavy diatomic molecules a main problem of using the Dirac equation as a zero approximation in molecular

calculations associated with the non-ability to divide the variables in difference of the standard non-relativistic Schrödinger equation.

In this paper on the basis of new gauge-invariant scheme in the relativistic energy approach combined with the multi-body perturbation theory for diatomic molecules it is formulated a new theoretical scheme for calculating the probabilities of radiative transitions of molecules. It is analysed the possible way to take into account for the inter-electron correlation and correspondingly the non-gauge-invariant contributions in relativistic molecular theory.

Naturally, one of the effective ways in relativistic molecular theory is in using the Breit-Pauli approximation [3-5].

2. Let us describe in brief the important moment of our theoretical approach. As usually, the wave functions zeroth basis is found from the Schrodinger (Dirac in the consistent version) equation solution with potential, which includes the core ab initio potential, electric potentials of nuclei and possibly exchange-correlation one-particle potentials. The last potential in part takes into account for contribution of the correlation corrections of the PT second and high orders (electrons screening, particle-hole interaction etc.) are accounted for.

For arbitrary diatomic molecule in the perturbation theory zeroth approximation the two-center centre Schrodinger equation is written in spheroidal coordinates, l,m,j

$$(\lambda = (r_A + r_B)/R, 1 \le \lambda < \infty,$$
$$\mu = (r_A - r_B)/R, -1 \le \mu \le 1,\ 0 \le \mu \le 2\pi)$$

and after a number of transformations results in the following form (look,for example, [5]):

$$[\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right) - \frac{m^2}{\lambda^2-1} - p^2\lambda^2 +$$
$$+ R(Z_A + Z_B - 2e^{-kR\lambda})\lambda + A] \times \Lambda(\lambda) = 0$$
$$[\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right) - \frac{m^2}{1-\mu^2} + p^2\mu^2 -$$
$$- R(Z_A - Z_B)\mu - A] \times M(\mu) = 0 \qquad (3)$$

where A is a constant separation. The wave function is represented as:

$$\psi(\lambda,\mu,\varphi) = \Lambda(\lambda)M(\mu,\varphi) = \Lambda(\lambda)G(\mu)e^{\pm im\varphi}. \qquad (4)$$

and the one-electron energy: $E = -2p^2/R^2$

The perturbation theory operator is as follows:

$$H_{\rho T} = \sum_{\delta}\sum_{ij}\left[r_{ij}^{-1} - V_M(r_{i\delta})\right] \qquad (5)$$

where d,i,j are the summation indexes correspondingly at nuclei and electrons.

In [5] it was constructed for the perturbation theory formalism for secular operator matrix and there are analyzed the diagrams summation tools for secular operator matrix. The terms of this set are represemted as contributions on of the Feynman diagrams, which are usually classified on number of the end lines. According to such a classification the matrix element of the secular operator has a form [5]:

$$M_{\xi\mu} = M_{\xi\eta}^{(0)} + M_{\xi\eta}^{(1)} + \ldots + M_{\xi\eta}^{(i)}, \qquad (6)$$

where i is a total number of valence particles, $M^{(0)}$ – the vacuum diagrams contribution (without the end lines) $M^{(1)}$ – a contribution of the 1-particles diagrams (one pair o the end lines); $M^{(2)}$-contribution of the two-particle diagrams (two pair of the end lines) and so on. Contribution $M^{(1)}$ is equal to a sum of the one-particle energies e_i. In the first perturbation theory order one should compute only the contribution of the two-particle diagrams of the first order. In fact this correction is equal to interaction energy of the particles $\Delta E^{(1)}$ and can be expressed through the matrix elements of the usual type on the wave functions of the zeroth approximation. For the Coulomb operator r_{12}^{-1} one should use the Neumann expansions on the Legendre polynomials of the first and second kind and spherical harmonics. 3.

3. As the first step, the relativistic block of the theory may into account the main relativistic effects within the model based on the perturbation theory with the Breit-Pauli Hamiltonian, taking into account relativistic corrections of the a^2 corder (a-fine structure constant), in particular,

the term due to the dependence of mass on velocity (H_1 and h_1), Darwin correction (H_2 and h_2), the spin-orbit term $\begin{bmatrix} H_3 & H_4 \\ h_3 & h_4 \end{bmatrix}$ [5]. The further simplification is connected with using the Cowan-Griffin approximation [13], which takes into account only two first effects in molecular calculations, in particular, for the s states.

Let us further examine the multielectron molecule with one or two quasi-particles (valence electrons). In the case of the multi-electron system with molecular core of the closed electron shells one can use the model potential method namely the bare two centre potential $V_N + V_C$ with V_N describing the electric potential of the nucleue, V_C, imitating the interaction of the quasi-particle with the molecular core. Surely, the core two-centre potential V_C is related to the core electron density r_C in a standard way. The latter fully defines the one electron representation. Moreover, all the results of the approximate calculations are the functionals of the density $r_C(r)$. The key step is determinatiojn of the complex energy of a molecule (that is in a relativistic theory).

According to the energy approach [17-19] the probability is directly connected with imaginary part of electron energy of the system, which is defined in the lowest order of perturbation theory as follows (the a-n transition is studied):

$$\mathrm{Im}\Delta E(B) = -\frac{e^2}{4\pi} \sum_{\alpha>n>f} V_{\alpha n \alpha n}^{|\omega_{\alpha n}|}; \qquad (5)$$

The matrix element in (5) is provided by the following determination:

$$V_{ijkl}^{|\omega|} = \iint dr_1 dr_2 \Psi_i^*(r_1)\Psi_j^*(r_2)\frac{\sin|\omega|r_{12}}{r_{12}}(1-\alpha_1\alpha_2)\Psi_k^*(r_2)\Psi_l^*(r_1) \qquad (6)$$

The separated terms of the sum in (5) represent the contributions of different channels and a probability of the dipole a-n transition is:

$$\Gamma_{\alpha_n} = \frac{1}{4\pi} \cdot V_{\alpha_n \alpha_n}^{|\omega_{\alpha_n}|} \qquad (7)$$

Under calculating the matrix elements (5) one could use the angle symmetry of the two-centre task and write the expansion for potential $\sin|w|r_{12}/r_{12}$ on spherical functions as follows [2]. This expansion is corresponding to usual multipole one for probability of radiative decay.

Obviously that the expression (5) is corresponding to first order of the molecular perturbation theory or second order of the quantum electrodynamical perturbation theory. Correspondingly in the second (fourth) order of the perturbation theory there are appeared the exchange-correlation or exchange-polarization corrections which being under consideration are gauge- dependent (dE_{ninv}) [19].

Surely, all the results of the exact calculation of any physical quantity must be gauge independent . However, even most advanced theories of diatomic molecules can hardly take into account all types of exchange-polarization corrections, especially, so called multi-particle ones and also continuum pressure etc. In fact their non-account provides a non-conservation of a gauge invariance in molecular calculations.

The simple way to reconstruct gauge invariance of a theory is to consider the corresponding many-particle exchange-polarization diagrams and determine the next corresponding term in an expression for the imaginary part of electron energy of the system (look different schemes in Refs. [20-25]). Then the minimization of the functional Im dE_{ninv} leads to the integro-differential equation for the r_c (the DF or Dirac-Kohn-Sham-like equations for the electron density) that should be numerically solved. In result there is a possibility to obtain the optimal one-particle representation and respectively optimal basis of electron orbitals, which is further used in calculation of the radiative transition characteristics.

Unlike the many-electron atoms in the case of diatomic molecules, this approach is naturally much more difficult. However, taking into account the substantial progress in the development of relativistic molecular theories, including, radiative transitions, the problem could be solved in a particular in simplifying accompanying approaches.

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Abstract.
On the basis of new gauge-invariant scheme in the relativistic energy approach combined with the multi-body perturbation theory for diatomic molecules it is formulated a new theoretical scheme for calculating the probabilities of radiative transitions of molecules. It is analysed the possible way to take into account for the inter-electron correlation and correspondingly the non-gauge-invariant contributions in relativistic molecular theory
Key words: radiative transitions, diatomic molecules, new relativistic approach

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А. В. Игнатенко, Е. Л. Пономаренко, А. С. Квасикова, Т. А. Кулакли

ОБ ОПРЕДЕЛЕНИИ ВЕРОЯТНОСТЕЙ РАДИАЦИОННЫХ ПЕРЕХОДОВ В РЕЛЯТИВИСТСКОЙ ТЕОРИИ ДВУХАТОМНЫХ МОЛЕКУЛ: НОВАЯ СХЕМА

Резюме.
С использованием калибровочно-инвариантной схемы в рамках релятивистского энергетического подхода и многочастичной теории возмущений для двухатомных молекул сформулирована новая теоретическая схему определения вероятностей радиационных переходов двухатом-

ных молекул. Предложены и проанализированы возможные методики учета обменно-корреляционных и соответственно, калибровочно-неинвариантных вкладов в вероятность перехода в релятивистской молекулярной теории.

Ключевые слова: радиационные переходы, двухатомные молекулы, новая релятивистская схема

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Г. В. Ігнатенко, Е. Л. Пономаренко, Г. С. Квасикова, Т. А. Кулакли

ПРО ВИЗНАЧЕННЯ ЙМОВІРНОСТЕЙ РАДІАЦІЙНИХ ПЕРЕХОДІВ У РЕЛЯТИВІСТСЬКІЙ ТЕОРІЇ ДВОАТОМНИХ МОЛЕКУЛ: НОВА СХЕМА

Резюме.

З використанням калібрувально-інваріантної схеми в рамках релятивістського енергетичного підходу і багаточастинкової теорії збурень для двохатомних молекул сформульована нова теоретична схему визначення ймовірностей радіаційних переходів двохатомних молекул. Запропоновані та проаналізовані можливі методики урахування обмінно-кореляційних і відповідно, калібрувально- неінваріантних внесків в ймовірність переходу в релятивістській молекулярній теорії.

Ключові слова: радіаційні переходи, двоатомні молекули, нова релятивістська схема