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There are presented key elements of modern quantum geometry and electrodynamics, namely, solutions of relativistic Dirac equation for electron in an external field, quantization of states of relativistic Dirac equation, quantum theory of electromagnetic radiation, mathematical formalism of a second quantization with application to configuration interaction quantum theory method and others. For M.Sc. and PhD students of the specialities: "Calculational Mathematics", "Optics and Laser Physics", "Mathematical Physics".

Изложены элементы современной квантовой геометрии и квантовой электродинамики, в частности, решение релятивистского уравнения Дирака для электрона во внешнем поле, квантование состояний релятивистского уравнения Дирака, квантовая теория электромагнитного излучения, математический аппарат вторичного квантования с применением к методу конфигурационного взаимодействия в квантовой теории и др. Для магистров и аспирантов специальностей «Вычислительная математика», «Оптика и лазерная физика», «Математическая физика».

Викладені елементи сучасної квантової геометрії та квантової електродинаміки, зокрема, рішення релятивістського рівняння Дірака для електрона у зовнішньому полі, квантування станів релятивістського рівняння Дірака, квантова теорія електромагнітного випромінювання, математичний апарат вторинного квантування із застосуванням до методу конфігураційної взаємодії в квантовій теорії тощо. Для магістрів та аспірантів спеціальностей «Обчислювальна математика», «Оптика та лазерна фізика», «Математична фізика».

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Introducing Remarks

Numerical (or calculational or computational) methods in quantum geometry and a chaos theory are central to modern computing mathematics and quantum physics and chemistry. It reflects new requirements that relate to modern mathematics and physics training.

It is well known that the methods of applied mathematics? Quantum geometry and mechanics give a powerful and and efficient tool researchers in various fields of science and engineering for mathematical modeling of the most difficult tasks . Especially this fact applies to address a wide range of problems of modern applied mathematics and computational physics. Implementation of new mathematical models on the computer is using methods of applied mathematics, which, of course, constantly being improved with advances in computer technology.

Construction of mathematical model of any problem, which is to ensure efficiency and optimality criterion, can be obtained quickly through an appropriate effective algorithm. Any reduction of problems of mathematical physics or engineering course often reduces to the solution of algebraic equations with one or other structure. As a result, most of the methods applied mathematics related to reducing the problem to a system of algebraic equations and their subsequent resolution.

In this book we present the key elements of of modern quantum geometry and electrodynamics, in particular, the solutions of the relativistic Dirac equation for an electron in an external field, quantization of states of the relativistic Dirac equation,quantum theory of electromagnetic radiation, mathematical formalism of the second quantization with application to configuration interaction quantum theory method and others.

For magisters and PhD students of the the specialities: "Calculational Mathematics", "Mathematical Physics".

Units. *Everywhere where otherwise indicated, atomic unitsare used:* e=1, $\hbar$=1, m=1. In these units: c=137,03597. Atomic units of length, time and velocity: $\hbar^2/me^2$=5,291773·10^{-11}m, $\hbar^3/me^4$=2,4189·10^{-17}s, $e^2/\hbar$=2,1877·10^{6} m/s. Atomic unit of energy (a.u.e.) $me^4/\hbar^2$=2Ry=27,2116eV=4,3598·10^{-18}J=2,19475·10^{5}cm^{-1}= 3,15780·10^{5} K (kelvin)=6,2709·10^{2} kcal/mole ($me^4/2\hbar^2$= Ry- Rydberg). Energy in Coulomb unts (c.u.): 1 c.u.e.= Z^2 a.u.e. (Z – charge of atomic nucleus). Relativistic units: $\hbar$=1, c=1, m=1, e^2=1/137,03597.

Abbreviations (used in the text):

AS- autoionization state,

CI - configuration interaction,

DF- Dirac-Fock (… method),

IS- isoelectronic sequence,

QED- quantum electrodynamics (…method),

LR- laser radiation,

MP- model potential,

MMP- method of model potential,

PP- pseudopotential,

MCA- multiconfiguration interation approximation,

PI- polarization interaction,

PC- polarization of the core,

PPI- potential of polarization interaction,

SCP- self-conjuction procedure,

OS- oscillator strength,

SSF- self-consistent field,

PT- perturbation theory,

DF- density functional,

HF- Hartree-Fock (…method),

SCE- screening effects.

Chapter 1

ELEMENTS OF QUANTUM GEOMETRY AND ELECTRODYNAMICS. QUANTIZATION OF STATES OF THE RELATIVISTIC DIRAC EQUATION

1.1 The relativistic Dirac equation for an electron in an external field

As is well known from QED (c.f. Classical Course of theoretical physics [1,2], we follow below) and quantum geometry (see. Eg., [3,4]), the wave equations of free particles express the properties that, In fact, the general requirements associated with the spatio-temporal symmetry. Naturally occurring particles is dependent on the physical properties of the processes of their interactions. Consistent description of electromagnetic interactions is given by one of the most reasonable physical theories - QED. Of course, it should be recalled that this formalism is used to describe the electromagnetic interactions of a particle is not capable of strong interactions. These particles, of course, are the electrons (and positrons), and thus, for the existing theory is available to the whole vast area electron QED.

Not capable of strong interactions also unstable particles - muons, τ-particles; they are described by the same QED in the phenomena occurring in times short compared to the duration of their life (due to the weak interactions). Standard electroweak theory is a generalization of QED, quantum theory of electromagnetic interactions. The assumption that there are weak forces in stable atoms, and as a consequence of parity violation in them - aspect of the electroweak theory, which is absent in QED.

QED - particularly well-founded and most thoroughly be tested physical theory. We have taken numerous experimental verification - always successful; in some cases, the accuracy of the agreement between experiment and theory reaches 10^{-10}. But, despite this, the tiny parity violation observed in atoms, can not be reconciled with QED. This - not a question of improving calculations or measurements.

Violation of mirror symmetry is simply incompatible with the fundamental hypotheses QED. It is interesting to recall that during the research question Fermi weak interaction in the process of absorption of light by atoms do not occur for a number of reasons. Firstly, weak interaction processes associated with the collapse (such as beta decay or K-capture), and stable atoms such processes naturally absent.

On the other hand, the weak interactions are extremely small compared to the range of atomic dimensions. Thus, either quantitatively or qualitatively even in times of Fermi could not imagine how weak interactions could affect the nuclear properties. It is well known, the electroweak theory generalizes QED in the so-called gauge theories in which the interaction between two particles occurs through the exchange of "gauge bosons" spin 1.

A classic example is given QED: the electromagnetic interactions are required to exchange photons - the most well-known gauge bosons. Since photons are electrically neutral, the charges of two interacting particles remain unchanged. Weak interactions through interaction of neutral currents and maintain a charge of interacting particles and transporting them boson (Z ° - boson) is also neutral.

The traditional range of tasks in quantum geometry and the theory of QED confined to a single particle. This is - the problem in which the number of particles does not change, and the interaction can be entered using the concept of an external electromagnetic field. In addition to the conditions that enable the external field is considered as a given, the limits of applicability of this theory are also limited conditions associated with so-called QED radiative corrections.

Following to Refs. [1-3], one could consider the wave equation of the electron in a given external field. As usual, let

$$A^{\mu} = (\Phi, \mathrm{A})$$

- 4-potential of the external electromagnetic field (A- vector, Φ- scalar potentials). Required equation follows from the Dirac equation by replacing the 4-momentum operator difference p-eA (e – particle charge):

$$[\gamma(p - eA) - m]\psi = 0 . \tag{1.1}$$

Here and below we use commonly used in relativistic QED units (see. below). where e^2 is replaced by α.

Corresponding to the Hamiltonian equation can also be obtained by replacing the standard Dirac Hamiltonian:

$$H = \alpha(p - eA) + \beta m + e\Phi\,. \tag{1.2}$$

It should be remembered that the invariance of the Dirac equation under a gauge transformation potential of the electromagnetic field is expressed in the fact that his views remain unchanged if at the same time with the transformation:

$$A \to A + ip\chi \tag{1.3}$$

(2.here χ - an arbitrary function) to convert the wave function according to

$$\psi = \psi e^{ie\chi}\,.$$

The current density is expressed in terms of the wave function using the formula of the form similar to $j = \bar{\psi}\gamma\psi$, the absence of an external electromagnetic field. Applying equation (1.1) the operation of charge conjugation, we have:

$$\bar{\psi}\left[\gamma\left(p + eA\right) + m\right] = 0\,, \tag{1.4}$$

Next is easy to rewrite this equation in the form:

$$\left[\tilde{\gamma}\left(p + eA\right) + m\right]\bar{\psi} = 0\,, \tag{1.5a}$$

and multiplying it by the matrix U_C on the left to find:

$$\left[\gamma\left(p + eA\right) - m\right]\left(C\psi\right) = 0\,. \tag{1.5б}$$

It should be noted that the charge-conjugate wave function satisfies the equation differs from the original by changing the sign of the charge. On the other hand, the operation of charge conjugation means the transition from particles to antiparticles. It follows the well-known conclusion, in particular, if the particles are electrically charged, the sign of the charge of the electron and positron are automatically opposed.

Let us now proceed to the consideration of the motion of an electron in a centrally symmetric electric field.

Of course, since the motion in a central field is stored angular momentum and parity (relative to the center of the field selected as the origin), the angular dependence of the wave functions of the spherical waves correspond to motion of free particles.

Naturally, this does not concern the form of radial wavefunctions. In connection with the above, the wave function of the stationary states (in the standard representation) must be sought in the form of:

$$\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} f(r)\Omega_{jlm} \\ (-1)^{\frac{1+l-l'}{2}} g(r)\Omega_{jl'm} \end{pmatrix}, \tag{1.6}$$

where

$$l = j \pm 1/2,\; l' = 2j - l\,,$$

and the exponent of -1 is introduced to simplify the subsequent formulas.

Dirac equation in the standard representation gives the following system of equations for φ and χ [1-3]:

$$(\varepsilon - m - U)\varphi = \sigma \mathrm{p}\chi\,, \tag{1.7}$$

$$(\varepsilon + m - U)\chi = \sigma \mathrm{p}\varphi\,, \tag{1.8}$$

where

$$U(r) = e\Phi(r) \tag{1.9}$$

- potential energy of the electron in the field.

The definition of the Dirac quantum number in the form:

$$\chi = \begin{cases} -\left(j+1/2\right) = -\left(l+1\right), & j = l+1/2, \\ +(j+1/2) = l, & j = l-1/2. \end{cases} \tag{1.10}$$

Recall quantum number χ takes all integer values, excluding the value of 0 (with positive numbers correspond to the case $j = l-1/2$, and the negative - the case $j = l+1/2$).

$$l\sigma = -\left(1+\chi\right), \tag{1.11}$$

so that

$$\left(\sigma\mathrm{p}\right)\chi = -\left(g' + \frac{1-\chi}{r} g\right) Q_{jlm}. \tag{1.12}$$

When this expression is substituted into the first equation of (1.7) spherical spinor Q_{jlm} in both sides of the equation is reduced (see details in [1,2]).

Conducting a similar transformation with the second equation can be as a result of the following system for radial Dirac functions:

$$f' + \frac{1+\chi}{r} f - \left(\varepsilon + m - U\right) g = 0, \tag{1.13}$$

$$g' + \frac{1-\chi}{r} g + \left(\varepsilon - m - U\right) f = 0, \tag{1.14}$$

or

$$\left(fr\right)' + \frac{\chi}{r}\left(fr\right) - \left(\varepsilon + m - U\right) gr = 0, \tag{1.15}$$

$$\left(gr\right)' - \frac{\chi}{r}\left(gr\right) + \left(\varepsilon - m - U\right) fr = 0, \tag{1.16}$$

The behavior of radial functions f and g at small distances is in many details considered in the Refs. [3,4].

1.2. Quantization condition of the Dirac equation for an electron in a Coulomb field

The quantization conditions of the Dirac equation for an electron in a Coulomb field are in details considered in Refs. [1-3]. Below it is important to consider a case of the field of attraction:

$$U = -Z\alpha/r\,. \tag{1.17}$$

or in conventional units:

$$U = -Ze^2/r \tag{1.18}$$

In relativistic units *ħ*=1, *c*=1, *m*=1, commonly used in QED, the square of the electron charge e^2 is replaced by the dimensionless α (1/α==137,03597).

For small r in equations (1.15,16) can be omitted from members $\varepsilon \pm m$ and then write:

$$(fr)' + \frac{\chi}{r} fr - \frac{Z\alpha}{r} gr = 0, \tag{1.19}$$

$$(\chi r)' - \frac{\chi}{r} gr + \frac{Z\alpha}{r} fr = 0. \tag{1.20}$$

Functions *fr* and *gr* are included in each of the above equations written equitable manner, so these functions are represented in equal degrees of *r*:

$$fr = ar^{\gamma}, \tag{1.21}$$

$$gr = br^{\gamma}. \tag{1.22}$$

Substitution into equation allows to get the famous formula:

$$\gamma^2 = \chi^2 - (Z\alpha)^2. \tag{1.23}$$

It is appropriate to recall that a purely Coulomb field can be considered only if the Dirac theory $Z\alpha<1$, ie $Z<137$.The charge $Z>137$ may actually be concentrated only in a "superheavy" nucleus of finite radius (see also chapter 3 of the book). Then for the function f one can have [3]:

$$f=\frac{Z\alpha}{\gamma+\chi}g=const\cdot r^{-1+\gamma},$$

$$\gamma=\sqrt{\chi^2-Z^2\alpha^2}=\sqrt{\left(j+1/2\right)^2-Z^2\alpha^2}\,. \tag{1.24}$$

Although the wave function and may apply at $r=0$ to infinity (if $\gamma<1$), integral of $|\psi|^2$ is, of course, converge. If $(Z\alpha)^2>\chi^2$, then both values γ from (1.22) - are imaginary. Appropriate decisions in $r\to 0$ oscillate as $r^{-1}\cos\left(|\gamma|\ln r\right)$), which again corresponds to the unacceptable situation in the relativistic theory "fall" to the center. Further, it is useful to exact solutions of the wave equation (G. Darwin, 1928; W. Gordon, 1928) as for the states of the discrete spectrum, and for continuum states [1-3].

Discrete spectrum $(\varepsilon<m)$. Convenient to look for functions f and g as:

$$f=\sqrt{m+\varepsilon}e^{-\rho/2}\rho^{\gamma-1}\left(Q_1+Q_2\right),$$

$$g=-\sqrt{m-\varepsilon}e^{-\rho/2}\rho^{\gamma-1}\left(Q_1-Q_2\right), \tag{1.25}$$

where there are introduced the notations

$$\rho=2\lambda r,$$
$$\lambda=\sqrt{m^2-\varepsilon^2},$$

$$\gamma=\sqrt{\chi^2-Z^2\alpha^2}\,.$$

This representation is naturally useful in connection with the behavior of functions for $\rho\to 0$ and exponential decay with $\rho\to\infty$.

After substituting (1.25) into (1.11) one can obtain the equations:

$$\rho\left(Q_1+Q_2\right)'+\left(\gamma+\chi\right)\left(Q_1+Q_2\right)-\rho Q_2+Z\alpha\sqrt{\frac{m-\varepsilon}{m+\varepsilon}}\left(Q_1-Q_2\right)=0,$$

$$\rho\left(Q_1-Q_2\right)'+\left(\gamma-\chi\right)\left(Q_1-Q_2\right)+\rho Q_2-Z\alpha\sqrt{\frac{m+\varepsilon}{m-\varepsilon}}\left(Q_1+Q_2\right)=0$$

(the prime denotes differentiation with respect to ρ) or, after elimination Q_1 or Q_2,

$$\rho Q_1''+\left(2\gamma+1-\rho\right)Q_1'-\left(\gamma-\frac{Z\alpha\varepsilon}{\lambda}\right)Q_1=0,$$

$$\rho Q_2''+\left(2\gamma+1-\rho\right)Q_2'-\left(\gamma+1-\frac{Z\alpha\varepsilon}{\lambda}\right)Q_2=0$$

When this is taken into account that:

$$\gamma^2-\left(Z\alpha\varepsilon/\lambda\right)^2=\chi^2-\left(Z\alpha m/\lambda\right)^2.$$

Solving these equations, finite at $\rho=0$ [1-3]:

$$Q_1=AF\left(\gamma-\frac{Z\alpha\varepsilon}{\lambda},\ 2\gamma+1,\ \rho\right), \tag{1.26}$$

$$Q_2=BF\left(\gamma+1-\frac{Z\alpha\varepsilon}{\lambda},\ 2\gamma+1,\ \rho\right), \tag{1.27}$$

where $F\left(\alpha,\ \beta,\ z\right)$- confluent hypergeometric function.

Communication between the constants *A* and *B*:

$$B = -\frac{\gamma - Z\alpha\varepsilon/\lambda}{\chi - Z\alpha\varepsilon/\lambda} A.$$

Both hypergeometric function in (1.27) should be limited to polynomials (otherwise they will grow at $\rho \to \infty$ as e^{ρ}, and with them will grow - as $e^{\rho/2}$ - and the whole wave function).

Function $F(\alpha, \beta, z)$ reduces to a polynomial if the parameter α is a negative integer or zero. Next is usually introduced notation:

$$\gamma - Z\alpha\varepsilon/\lambda = -n_r. \tag{1.28}$$

If $n_r = 1, 2, ...$, then two hypergeometric functions reduce to polynomials. If $n_r = 0$, then reduces to the polynomial only one of them. But equality $n_r = 0$ means $\gamma = Z\alpha\varepsilon/\lambda$, and then

$$Z\alpha m/\lambda = |\chi|$$

If $\chi < 0$, then coefficient B (1.7) vanishes, so that $Q_2 = 0$, and the required condition is not violated. If $\chi > 0$, then $B = -A$, and Q_2 remains at $n_r = 0$ a divergent function. As a result, the following values of the quantum number n_r:

$$n_r = \begin{cases} 0, 1, 2, ... \ npu \ \chi < 0; \\ 1, 2, 3, ... \ npu \ \chi > 0. \end{cases} \tag{1.29}$$

It follows the familiar expression (Sommerfeld formula) for the discrete energy levels:

$$\frac{\varepsilon}{m} = \left[1 + \frac{(Z\alpha)^2}{\left(\sqrt{\chi^2 - (Z\alpha)^2} + n_r \right)^2} \right]^{-1/2}. \tag{1.30}$$

At $Z\alpha$~1 the first terms of the expansion of the formula (1.30) are well known form:

$$\frac{\varepsilon}{m}-1=-\frac{(Z\alpha)^2}{2\left(|\chi|+n_r\right)^2}\left\{1+\frac{(Z\alpha)^2}{|\chi|+n_r}\left[\frac{1}{|\chi|}-\frac{3}{4\left(|\chi|+n_r\right)}\right]\right\}.$$

The last formula makes sense in its exact form at $Z\alpha$~1. It is also important to recall that in (1.30) contains a twofold degeneracy of levels (it includes only $|\chi|$, with different levels of l at the same j still the same). The lifting of degeneracy is provided by radiative (QED) corrections.

This is followed to determine the overall normalization factor A in the wave function, as the wave function of the discrete spectrum must be normalized by the condition:

$$\int |\psi|^2 d^3x = 1$$

$$\int \left(f^2+g^2\right) r^2 dr = 1.$$

The final expression for the normalized wave functions have the form [1]:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} = \frac{\pm(2\lambda)^{3/2}}{\Gamma(2\gamma+1)}\left[\frac{(m\pm\varepsilon)\Gamma(2\gamma+n_r+1)}{4m\frac{Z\alpha m}{\lambda}\left(\frac{Z\alpha m}{\lambda}-\chi\right)n_r!}\right]^{1/2}(2\lambda r)^{\gamma-1}e^{-\lambda r}\times$$
$$\times\left\{\left(\frac{Z\alpha m}{\lambda}-\chi\right)F\left(-n_r,2\gamma+1,2\lambda r\right)\mp n_r F\left(1-n_r,2\gamma+1,2\lambda r\right)\right\} \tag{1.31}$$

(upper signs refer to *f*, lower – to *g*).

Continuous spectrum $(\varepsilon > m)$. The wave functions of this case can be obtained from the discrete spectrum replacement:

$$\sqrt{m-\varepsilon} \to -i\sqrt{\varepsilon - m},$$

$$\lambda \to -ip,$$

$$-n_r \to \gamma - i\frac{Z\alpha\varepsilon}{p}. \qquad (1.32)$$

The only thing that needs to be addressed - this normalization functions.

Replacement (1.31) allow us to represent the functions f and g in the form:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} = \left.\begin{matrix} \sqrt{\varepsilon+m} \\ i\sqrt{\varepsilon-m} \end{matrix}\right\} \cdot A' e^{ipr}\left(2pr\right)^{\gamma-1} \times$$
$$\times\left[e^{i\xi}F\left(\gamma - iv,\ 2\gamma+1,\ -2ipr\right) \mp e^{-i\xi}F\left(\gamma+1-iv,\ 2\gamma+1,\ -2ipr\right)\right], \qquad (1.33)$$

where A' - new normalization constant and introduced the notation

$$v = \frac{Z\alpha\varepsilon}{p}, \qquad (1.34)$$

$$e^{-2i\xi} = \frac{\gamma - iv}{\chi - ivm/\varepsilon} \qquad (1.35)$$

Here, of course, the value ξ is real, because

$$\gamma^2 + \left(Z\alpha\varepsilon/p\right)^2 = \chi^2 + \left(Z\alpha m/p\right)^2). \qquad (1.36)$$

The final expression for the wave functions of the continuous spectrum has the form:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} = 2^{3/2}\sqrt{\frac{m\pm\varepsilon}{\varepsilon}}e^{\frac{\pi v}{2}}\frac{\left|\Gamma\left(\gamma+1+iv\right)\right|}{\Gamma\left(2\gamma+1\right)}\frac{\left(2pr\right)^{\gamma}}{r}\times$$
$$\times \begin{matrix}\mathrm{Im}\\ \mathrm{Re}\end{matrix}\left\{e^{i\left(pr+\xi\right)}F\left(\gamma-iv,2\gamma+1,-2ipr\right)\right\}. \tag{1.37}$$

Asymptotic expression for this function:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} = \frac{\sqrt{2}}{r}\sqrt{\frac{\varepsilon\pm m}{\varepsilon}}\begin{matrix}\sin\\ \cos\end{matrix}\left\{pr+\delta_{\chi}+v\ln 2pr-\frac{\pi l}{2}\right\}, \tag{1.38}$$

where

$$\delta_{\chi} = \xi - \arg\Gamma\left(\gamma+1+iv\right) - \frac{\pi\gamma}{2} + \frac{\pi l}{2}, \tag{1.39}$$

or

$$e^{2i\delta_{\chi}} = \frac{\chi - ivm/\varepsilon}{\gamma - iv}\frac{\Gamma\left(\gamma+1-iv\right)}{\Gamma\left(\gamma+1+iv\right)}e^{i\pi\left(l-\gamma\right)}. \tag{1.40}$$

1.3 Elements of quantum geometry and quantum theory of electromagnetic adiation.

In view of the smallness of the fine structure constant $\alpha = e^2/\hbar c = 1/137$ (more precisely: $1/\alpha$ == 137,03597) compared to 1, which plays a fundamental role in QED and characterizing the intensity of the electromagnetic interaction, of course, the interaction of electrons with the electromagnetic field can be viewed by PT.

Recall that in the early 70s Hooft [1] showed that the electroweak theory of Glashow-Weinberg-Salam also be considered as part of a coordinated PT mathematically it in any way that, in fact, is the basis of application of the PT to the description of the electroweak interaction.

In classical electrodynamics the electromagnetic interaction is described by the well-known expression:

$$-ej^{\mu}A_{\mu} \tag{1.41}$$

density langranzhiana "field + charges" (A - 4-potential field j - 4-vector current density of the particles). The current density satisfies the continuity equation:

$$\partial_{\mu} j^{\mu} = 0, \tag{1.42}$$

expresses the law of conservation of charge.

The gauge invariance of the theory is closely connected with this law. As is well known [1-3] by replacing

$$A_{\mu} \to A_{\mu} + \partial_{\mu}\chi$$

to Lagrangian density (2.1.41) added value $-ej^{\mu}\partial_{\mu}\chi$, which in view of (1.42) can be represented in the form of 4-divergence

$$-e\partial_{\mu}\left(\chi j^{\mu}\right)$$

and therefore falls in the integration over d^4x in action:

$$S = \int L d^4 x \, .$$

Recall that the usual QED 4-vectors $\vec{j}$ and $\vec{A}$ replaced by the corresponding second-quantized operators.

In this case, the current operator is expressed through the ψ-operators in accordance with:

$$\hat{j} = \overline{\psi} \gamma \psi \ .$$

The role of generalized "coordinates" in Lagrangian (2.see Classical mechanics)

$$\int \hat{L}_{\text{int}} d^3 x = -e \int \left(\hat{j} A \right) d^3 x \qquad (1.43a)$$

play $\overline{\psi}, \psi, A$ in each point of space.

Lagrangian density depends only on themselves "coordinates" q (but not their derivatives x), so the transition to the Hamiltonian density is reduced only to a change in the sign of the Lagrangian density.

The electromagnetic interaction operator (the integral over the space of the interaction Hamiltonian density) has the standard form:

$$V_{\text{int}} = e \int \left(\hat{j} A \right) d^3 x \, . \qquad (1.43б)$$

The operator of the free electromagnetic field is the sum of

$$A = \sum_n \left[\hat{c}_n A_n (x) + \hat{c}_n^+ A_n^* (x) \right], \qquad (1.44)$$

containing the creation and annihilation operators of photons in different states

(2.numbered index n).

The probability of transition in the quantum system under the influence of the perturbation V_{int} in the first approximation is given by the formula known PT ("golden" rule by Fermi).

It is usually assumed that the initial and final states of the radiating system belong to the discrete spectrum. Then the probability (per unit time) of the transition $i \to f$ with the emission of a photon is given by the well-known formula:

$$d\omega = 2\pi \left|V_{fi}\right|^2 \delta\left(E_i - E_f - \omega\right) dv, \tag{1.45}$$

where v conventionally denotes the set of variables that characterize the state of the photon and runs through a continuous range of values (in this case the photon wave function is assumed normalized to δ-function "scale v").

If the photon is emitted with a certain value of the moment, the only variable is the continuous frequency ω. Integration of the formula (1.45) to $dv \equiv d\omega$ eliminate δ-function (replacing ω the value $\omega = E_i - E_f$), and then the transition probability is determined simply by the expression:

$$\omega = 2\pi \left|V_{fi}\right|^2. \tag{1.46}$$

If we consider the emission of a photon with a given momentum ***k***, then

$$dv = d^3k \big/ \left(2\pi\right)^3 = \omega^2 d\omega\, do \big/ \left(2\pi\right)^3 .$$

It is assumed that the photon wave function (plane wave) is normalized to one photon in the volume $V = 1$ and dv - the number of states have accounted for the phase volume Vd^3k.

As a result, the probability of emission of a photon with a given momentum can obtain the following well-known expression:

$$d\omega = 2\pi \left|V_{fi}\right|^2 \delta\left(E_i - E_f - \omega\right) \frac{d^3k}{\left(2\pi\right)^3}, \tag{1.47}$$

or after integration by $d\omega$:

$$d\omega = \frac{1}{4\pi^2} \left|V_{fi}\right|^2 \omega^2 do. \tag{1.48}$$

As V_{fi} in (1.8) is substituted matrix element of the form:

$$V_{fi} = e\sqrt{4\pi} \frac{1}{\sqrt{2\omega}} e_\mu^* j_{fi}^\mu \left(k\right). \tag{1.49}$$

Further, it is useful to formula relating to dipole radiation. Recall E1 radiative transitions are the most intense in the atomic spectra, and M1 - respectively in nuclear systems. Transition current in this case is the matrix element of the operator

$$\hat{j} = \bar{\psi}\gamma\psi ,$$

in which the ψ-operators are assumed to expansions in the wave functions of the stationary states of the electron in this field.

Such a change in the occupation numbers by the operator $\overset{+}{a}_f a_i$, and the transition current expression is valid:

$$j_{fi}^\mu = \bar{\psi}_f \gamma^\mu \psi_i = \left(\psi_f^* \psi_i, \psi_f^* \alpha \psi_i\right), \tag{1.50}$$

where ψ_i and ψ_f - the wave functions of the initial and final states of the electron.

The key point of any theory of radiative transitions - the choice of gauge photon propagator. Following [1], we choose the wave function of a photon in a three-dimensionally transverse gauge (polarization 4-vector $e = \left(0, \mathrm{e}\right)$).

Then (1.49) the multiplication:

$$j_{fi}e^* = -\mathrm{j}_{fi}e^*.$$

Substitution V_{fi} in (1.48) gives the well-known expression for the probability of radiation into the solid angle do of a photon with polarization e:

$$d\omega_{en} = e^2 \frac{\omega}{2\pi} \left| \mathrm{e}^* \mathrm{j}_{fi}(\mathrm{k}) \right|^2 do, \tag{1.51}$$

where

$$\mathrm{j}_{fi}(\mathrm{k}) = \int \psi_f^* \alpha \psi_i e^{-i\mathrm{kr}} d^3x. \tag{1.52}$$

Here the summation over photon polarizations is done by averaging over the directions of **e** (in a plane perpendicular to a given direction $\mathrm{n} = \mathrm{k}/\omega$) and then the result is multiplied by 2, respectively, to two independent features transverse photon polarization.

As a result, the final expression takes the form:

$$d\omega_n = e^2 \frac{\omega}{2\pi} \left| \left[\mathrm{n}\mathrm{j}_{fi}(\mathrm{k}) \right] \right|^2 do. \tag{1.53}$$

It is appropriate to recall that, as a rule, first consider the case where the photon wavelength λ large compared with the size of the radiating system a and that is usually associated with the smallness of the particle velocities compared to the speed of light (see details in Refs. [1-4]).

In the first approximation in a/λ (corresponding to dipole radiation) in the current transition (1.52) factor $e^{-i\mathrm{kr}}$ (varies little in the area where ψ_i or ψ_f significantly different from zero) for obvious reasons, is replaced by 1.

Further, the integral $\mathrm{j}_{fi}(0)$ can be replaced by its non-relativistic expression, ie, a matrix element v_{fi} of the electron velocity with respect to the Schrödinger wave functions. Seeking matrix element can be expressed as:

$$v_{fi} = -i\omega \mathrm{r}_{fi}\,,$$

and

$$e\mathrm{r}_{fi} = \mathrm{d}_{fi}\,,$$

where **d** - the dipole moment of the electron (in its orbital motion).

As a result, we can come to the following classical formula for the probability of dipole radiation [1,2]:

$$d\omega_{en} = \frac{\omega^3}{2\pi}\left|\mathrm{e}^*\mathrm{d}_{fi}\right|^2 do \tag{1.54}$$

(and direction **n** appears here in an implicit form: vector **e** must be perpendicular to **n**).

Summation over polarizations gives [1,2]:

$$d\omega_n = \frac{\omega^3}{2\pi}\left|\left[\mathrm{n}\mathrm{d}_{fi}\right]\right|^2 do\,. \tag{1.55}$$

Under d_{fi} here obviously refers to a matrix element of the dipole moment of the complete system.

Integration of the formula (1.55) in all directions allows to obtain the following well-known expression for the total probability of radiation [1,2]:

$$\omega = \frac{4\omega^3}{3}\left|\mathrm{d}_{fi}\right|^2, \tag{1.56}$$

In conventional terms, this formula has the form:

$$\omega = \frac{4\omega^3}{3\hbar c^3}\left|\mathrm{d}_{fi}\right|^2. \tag{1.57}$$

Recall that the radiation intensity I is obtained by multiplying the probability for $\hbar\omega$ that is [1,2]

$$I = \frac{4\omega^4}{3c^3}\left|\mathrm{d}_{fi}\right|^2 . \tag{1.58}$$

It is useful to note that the above formulas are completely analogous to the known classical formulas (classical electrodynamics) for the intensity of dipole radiation system periodically moving particles: the intensity of the radiation frequency $\omega_s = s\omega$ (where ω - the frequency of the motion of particles, s - an integer) is

$$I = \frac{4\omega_s^4}{3c^3}\left|\mathrm{d}_s\right|^2 , \tag{1.59}$$

where d_s - the Fourier components of the dipole moment, i.e., expansion coefficients

$$\mathrm{d}(t) = \sum_{s=-\infty}^{\infty} \mathrm{d}_s e^{-is\omega t} \quad . \tag{1.60}$$

Next, it is important to present the elements of the theory of electric and magnetic multipole radiation, following to Refs.[1-3].

In the light of the material presented above, it is convenient to restrict in this section considering the emission of a photon with definite values of the angular momentum j and its projection m on a chosen direction.

As is known, such photons can be of two types - electric and magnetic. Consider the electric multipole radiation.

We assume that the size of the radiating system are small compared with the wavelength. Following [1-3], it is possible to perform all the calculations using the photon wave functions in the momentum representation, ie, presenting a 4-vector $A^{\mu}(\mathrm{r})$ in the form of a Fourier integral.

The transition matrix element is [1-3]:

$$V_{fi}=e\int j^{\mu}_{ji}(\mathrm{r})A^{*}_{\mu}(\mathrm{r})d^{3}x=e\int d^{3}x\cdot j^{\mu}_{fi}(\mathrm{r})\int\frac{d^{3}k}{(2\pi)^{3}}A^{*}(\mathrm{r})e^{-ikr} \quad (1.61)$$

In order to simplify the notation is convenient to omit the indices ωjm of the photon wave functions. Next to Ej-photon use wave function (2.vector potential) [1-3]:

$$\vec{A}^{\text{э}}_{\omega jm}(\vec{k})=\frac{4\pi^{2}}{\omega^{3/2}}\delta(|\vec{k}|-\omega)(\vec{Y}^{\text{э}}_{jm}+C\vec{n}Y_{jm}) \quad (1.62)$$

$$\Phi^{(\text{э})}_{\omega jm}(\vec{k})=\frac{4\pi^{2}}{\omega^{3/2}}\delta(|\vec{k}|-\omega)CY_{jm}$$

with an arbitrary gauge constant *C* equal to, say,

$$C=-\sqrt{\frac{j+1}{j}}\ .$$

With this choice in the spatial components of the wave function (A) is reduced members comprising spherical harmonics of order $j-1$ and, accordingly, $\vec{A}^{\text{э}}_{\omega jm}$ comprises only the order of spherical harmonics $j+1$, resulting in the corresponding contribution V_{fi} is higher order (in a/λ) than the contribution from the components $A^{0}\equiv\Phi$, containing spherical functions of lower order j. That is, it should be:

$$A^{\mu}=(\Phi,0),$$

$$\Phi=-\sqrt{\frac{j+1}{j}}\frac{4\pi^{2}}{\omega^{3/2}}\delta(|\mathrm{k}|-\omega)Y_{jm}(\mathrm{n})$$

(is there $\mathrm{n}=\mathrm{k}/\omega$).

After the known transofrmations one could get as follows [1-3]:

$$V_{fi} = -e\sqrt{\frac{j+1}{j}}\,\frac{\sqrt{\omega}}{2\pi}\int d^3x\cdot\rho_{fi}\left(\mathrm{r}\right)\int do_{\mathrm{n}}e^{-ikr}Y^{*}_{jm}\left(\mathrm{n}\right). \qquad (1.63)$$

Usually to calculate the inner integral is used decomposition [1,2], one uses the expansion:

$$e^{ikr} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l g_l\left(kr\right)Y^{*}_{lm}\left(\frac{\mathrm{k}}{r}\right)Y_{lm}\left(\frac{\mathrm{r}}{r}\right), \qquad (1.64)$$

where

$$g_l\left(kr\right) = \sqrt{\frac{\pi}{2kr}}J_{l+1/2}\left(kr\right). \qquad (1.65)$$

In view of the condition $a/\lambda \ll 1$ in the integral d^3x over a distance play a role for which $kr \ll 1$. In such cases, usually functions $g_j\left(kr\right)$ are replaced by the first terms of their expansions in kr, i.e.:

$$g_j\left(kr\right) \approx \frac{\left(kr\right)^j}{\left(2j+1\right)!!}. \qquad (1.66)$$

The final expression for the matrix element of the transition is as follows [1-3]:

$$V_{fi} = \left(-1\right)^{m+1} i^j \sqrt{\frac{\left(2j+1\right)\left(j+1\right)}{\pi j}}\,\frac{\omega^{j+1/2}}{\left(2j+1\right)!!}\,e\left(Q^{(\text{э})}_{j,-m}\right)_{fi}. \qquad (1.67)$$

Here it is added the value of $Q^{(2.\text{э})}$, which are commonly referred to as 2^j-dipole electric moments of transition of the system, by analogy with corresponding classical values [1,2]:

$$\left(Q^{(\text{э})}_{jm}\right)_{fi} = \sqrt{\frac{4\pi}{2j+1}}\int \rho_{fi}\left(\mathrm{r}\right)r^j Y_{jm}\left(\frac{\mathrm{r}}{r}\right)d^3x \qquad (1.67)$$

For an electron in the external field $\rho_{fi} = \psi_f^* \psi_i$, and then the value (1.67) are calculated as the matrix elements of the classical values:

$$Q_{jm}^{(\text{э})} = \sqrt{\frac{4\pi}{2j+1}}\, r^j Y_{jm}. \tag{1.68}$$

The above expression for the wave function of the photon corresponds to the normalization δ-function ω scale. Then, after substituting it into (1.7) for the probability of Ej - radiation turns well-known formula [1-3]:

$$\omega_{jm}^{(\text{э})} = \frac{2(2j+1)(j+1)}{j\left[(2j+1)!!\right]^2}\, \omega^{2j+1} e^2 \left| \left(Q_{j,-m}^{(\text{э})} \right)_{fi} \right|^2 . \tag{1.69}$$

The angular distribution of multipole radiation is given by [1-3]:

$$d\omega_{jm} = \left| \mathrm{Y}_{jm}^{(\text{э})}(\mathrm{n}) \right|^2 \omega_{jm} do = \frac{\omega_{jm}}{j(j+1)} \left| \nabla_{\mathrm{n}} Y_{jm} \right|^2 do . \tag{1.70}$$

If the order of magnitude of the size of the system (atom and the nucleus) is a, then the order of magnitude of the electric multipole moments is, generally speaking $Q_{jm}^{(\text{э})} \sim a^j$. The probability of multipole radiation:

$$\omega_{jm}^{(\text{э})} \sim \alpha k (ka)^{2j} \tag{1.71}$$

i.e. increase in the degree multpolnosti 1 reduces the probability of emission with respect to ~$(ka)^2$.

The most important aspect of the theory - the selection rules for transitions of the corresponding type [1,2]. Recall, that the laws of conservation of momentum and parity lead to certain selection rules, limits the possibility of changing the state of the radiating system.

If the starting point of the system is J_i, after the emission of a photon with momentum j moment of the system can take only the values of J_f, determined by the rules of addition of moments ($| J_i - J_f | = j$):

$$|J_i - J_f| \leq j \leq J_i + J_f\,. \tag{1.72}$$

Projection M_i and M_f points J_i and J_f together with the projection m of the photon satisfy the rule (of the same law of addition of points):

$$M_i - M_f = m\,. \tag{1.73}$$

Parity P_i and P_f initial and final states of the radiating system must satisfy the condition $P_f P_\Phi = P_i$ where P_Φ - the parity of the emitted photon; For the photon electric type $P_\Phi = (-1)^j$, hence the parity selection rules for electric multipole radiation:

$$P_i P_f = (-1)^j\,. \tag{1.74}$$

The selection rules for the total angular momentum and parity are quite strict and must be observed in the emission of any system.

The total probability of $M1$-radiation expressed in terms of this value by the standard formula (in conventional units):

$$\omega = \frac{4\omega^3}{3\hbar c^3}\left|\mu_{fi}\right|^2. \tag{1.75}$$

The expression for μ_{fi} becomes [1-3]:

$$\mu_{fi} = \int \psi_f^* \left(\frac{e}{2m}\hat{\mathbf{L}} + \frac{\mu}{s}\hat{\mathbf{s}} \right) \psi_i d^3x\,, \tag{1.76}$$

where $\hat{\mathbf{L}} = -i[r\nabla]$- the operator of the orbital angular momentum of the particle. That is, as you might expect, μ_{fi} is a matrix element of the operator:

$$\hat{\boldsymbol{\mu}} = \frac{e}{2m}\hat{\mathbf{L}} + \frac{\mu}{s}\hat{\mathbf{s}}\,, \tag{1.77}$$

representing the sum of the operators of the orbital and intrinsic magnetic moment of the particle.

The selection rules for the magnetic multipole radiation similar to the rules for the electric case, in particular, for parity it is true the rule:

$$P_i P_f = \left(-1\right)^{j+1}, \tag{1.78}$$

obtained by substituting parity *Mj*-photon: $P_{\phi} = \left(-1\right)^{j+1}$.

Chapter 2

CONFIGURATION INTERACTION IN THE SECOND QUANTIZATION REPRESENTATION: BASICS WITH APPLICATIONS UP TO FULL CI

2.1. Introduction

Here the mathematical formalism of the second quantization is applied to the configuration interaction (CI) method in quantum chemistry. Application of the Wick's theorems for calculation of the matrix elements over configurations leads to a simple logical scheme which is valid for configurations of an arbitrary complexity and can be easily programmed.

The main advantage of the configuration interaction (CI) method [5] is the possibility of improving a trial wave function by extending considerably a set of basis configurations. The simple analytical expressions for the matrix elements of the Hamiltonian over the singly excited singlet and triplet configurations are well known. Thus an interaction of these configurations became a standard method for computing excited states of molecules. Similarly, an interaction between singly excited configurations is frequently used for the calculation of the electronic structure of radicals, while doubly excited configurations have been still used occasionally. Finally, not much is still known about contributions of configurations involving an excitation of three and more electrons.

Development of the expressions for the CI matrix elements can be considerably simplified when the second quantization formalism [5] is used instead of the usual method based on superposition of determinants (see also Appendix).

The former approach has been used in order to obtain the matrix elements over the doubly excited singlet configurations [6]. A comparison with the corresponding elements over singly excited configurations shows that the expressions for the CI matrix elements become progressively complicated as configurations become more complex.

The necessity to include more and more complicated formulae into the computer program is the main obstacle to a wider use of the extended configuration sets. In order to overcome these difficulties it is necessary to abandon the derivation of the analytical expressions for the matrix elements and to delegate this work to a computer at an early stage of the calculation. The simple rules to compute the matrix elements in the second quantization representations which follow from Wick's theorem [7] and are also good for configurations of an arbitrary complexity need to be programmed. The present review is devoted to an actual realization of the above suggestion [8, 9]. Since the second quantization formalism has been described by many authors [5] we shall give only those formulae and statements which are necessary for our discussion.

In CI computations one first includes those configurations which do not differ much from the ground configuration. For example, the singly excited configurations are constructed from the Slater determinants built from the ground state determinant by changing a single row. To account for only the changes in an explicit form in the many-particle SCF theory, an elegant mathematical apparatus known as hole formalism has been developed. Besides offering a simple physical interpretation, the hole formalism reduces the calculations considerably. This formalism generalized on an arbitrary orthonormal orbital set will be exposed below.

2.2 The Second Quantization and CI Method

Let us consider a system of electrons in an external field, e.g. in a field of fixed nuclei. The Hamiltonian of this system is represented by a sum of one electron operators $\hat{h}(k)$, each of which acts on coordinates of one of the electrons and contains its kinetic energy operator and the external field potential, and a sum over all possible pairs of electrons of the electron interaction operators $\hat{U}(k,l)$.

Let be given a complete orthonormal set of orbitals $\varphi_1, \varphi_2, \varphi_3, \ldots$. Multiplying each orbital φ_i in turn by the spin functions η_+ and η_- which are eigenfunctions of the spin angular momentum operator with the eigenvalues $+1/2$ and $-1/2$ (in units of $\hbar$) one obtains a complete orthonormal system of spin orbitals $\psi_{i\sigma}$:

$$\psi_{1+}, \psi_{1-}, \psi_{2+}, \psi_{2-}, \psi_{3+} . \psi_{3-}, \cdots ,$$

where

$$\psi_{i+} = \varphi_i \eta_+ , \psi_{i-} = \varphi_i \eta_- .$$

In order to pass to the second quantization representation we shall now introduce creation $\hat{A}^+_{i\sigma}$ and annihilation $\hat{A}_{i\sigma}$ operators for an electron in a state $\psi_{i\sigma}$. They obey anticommutation relations

$$\left[\hat{A}^+_{i\sigma}, \hat{A}^+_{j\sigma'} \right]_+ = \left[\hat{A}_{i\sigma}, \hat{A}_{j\sigma'} \right]_+ = 0 , \; \left[\hat{A}_{i\sigma}, \hat{A}^+_{j\sigma'} \right]_+ = \delta_{ij} \delta_{\sigma\sigma'} . \tag{2.1}$$

The many-electron spin-free Hamiltonian is then given by

$$\hat{H} = \sum_{ij\sigma} \hat{A}^+_{i\sigma} \hat{A}_{j\sigma} h_{ij} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} (ij \,|\, kl) \, \hat{A}^+_{i\sigma} \hat{A}^+_{j\sigma'} \hat{A}_{l\sigma'} \hat{A}_{k\sigma} , \tag{2.2}$$

where

$$h_{ij} = \left\langle \varphi_i \,|\, \hat{h} \,|\, \varphi_j \right\rangle , \tag{2.3}$$

$$(ij \,|\, kl) = \left\langle \varphi_i \varphi_j \,|\, \hat{U} \,|\, \varphi_k \varphi_l \right\rangle . \tag{2.4}$$

Operators in the second quantization representation, including the Hamiltonian (2.2), act in a linear space, say R, with basis which can be constructed in the following way. First, one introduces a vacuum state vector $|0\rangle$ defined for all i and σ by

$$\hat{A}_{i\sigma} |0\rangle = 0 , \; \langle 0 | \hat{A}^+_{i\sigma} = 0 \tag{2.5}$$

with the vacuum state supposed to be normalized

$$\langle 0 | 0 \rangle = 1 . \tag{2.6}$$

Acting on the vacuum state by each of the creation operator one obtains all one-particle states

$$|i\sigma\rangle = \hat{A}^{+}_{i\sigma}|0\rangle\,. \tag{2.7}$$

The states with two electrons are generated by operator $\hat{A}^{+}_{j\sigma'}$ acting on the state $|i\sigma\rangle$

$$|\,j\sigma', i\sigma\rangle = \hat{A}^{+}_{j\sigma'}|i\sigma\rangle = \hat{A}^{+}_{j\sigma'}\hat{A}^{+}_{i\sigma}|0\rangle\,. \tag{2.8}$$

It follows from the anticommutation relations (2.1) that only those vectors are linearly independent and not equal to zero for which $i = j$ and $\sigma = \sigma'$ are not valid simultaneously.

Following this procedure we obtain a set of linearly independent states with an arbitrary number of electrons

$$|\,p\sigma\rangle = \hat{A}^{+}_{p_1\sigma_1}\hat{A}^{+}_{p_2\sigma_2}\hat{A}^{+}_{p_3\sigma_3}\cdots\hat{A}^{+}_{p_N\sigma_N}|0\rangle\,, \tag{2.9}$$

where symbol p covers a totality of numbers $p_1, p_2, p_3, ..., p_N$, and symbol σ – a totality of numbers $\sigma_1, \sigma_2, \sigma_3, ..., \sigma_N$, and if $p_n = p_{n+1}$ then $\sigma_n > \sigma_{n+1}$. A set of all these states with $N = 1, 2, 3, ...$ determines the basis we have wished to construct.

Using the anticommutation relations (2.1) and definitions (2.5) and (2.6) one can show that each of the basis vectors is an eigenvector of an operator

$$\hat{N} = \sum_{i\sigma}\hat{A}^{+}_{i\sigma}\hat{A}_{i\sigma} \tag{2.10}$$

with an eigenvalue N.

The Hamiltonian (2.2) commutes with the number-of-particles operator $\hat{N}$ and each one of its eigenvectors belongs to one of the subspaces R_N of the space R built on the basis vectors with definite N. For this reason we fix a number of particles N in our system and will construct corresponding eigenvectors.

The expansion coefficients of the eigenvectors of $\hat{H}$ over the basis vectors are usually determined as solutions of the eigenvalue problem for a matrix with the elements $\langle p'\sigma' | \hat{H} | p\sigma \rangle$.

For the practical determination of approximate eigenvectors the CI matrix is truncated before diagonalization. The order of the CI matrix which is to be diagonalized can be decreased considerably if there are operators which commute with the Hamiltonian as well as between each other.

Then using an appropriate unitary transformation one goes from the set of vectors $| p\sigma \rangle$ to a new set of the basis vectors which are eigenvectors of these operators, and an initial eigenvalue problem reduces into several eigenvalue problems of a smaller order. Each of them corresponds to a definite totality of eigenvalues of the operators mentioned.

The spin-free Hamiltonian always commutes with the total spin projection operator $\hat{S}_z$ and with the square of the total spin operator $\hat{S}^2$. These two operators commute with each other also. We shall first find the expressions for them both in the second quantization representation. Expression for $\hat{S}_z$ is obtained from the general definition of an one-particle operator

$$\hat{Q} \equiv \sum_{ij\sigma\sigma'} \hat{A}^+_{i\sigma} \hat{A}_{j\sigma'} < \psi_{i\sigma} | \hat{Q} | \psi_{j\sigma'} >, \qquad (2.11)$$

where one should place $\hat{Q} = \hat{S}_z$. Using the orthonormality of the spin-orbitals and the definition

$$\hat{S}_z \psi_{i\sigma} = \frac{1}{2} \sigma \psi_{i\sigma}$$

one obtains

$$\hat{S}_z = \frac{1}{2} \sum_{i\sigma} \sigma \hat{A}^+_{i\sigma} \hat{A}_{i\sigma} . \qquad (2.12)$$

To construct an operator $\hat{S}^2$ we begin with the well known Dirac expression [10]

$$\hat{S}^2 = \frac{1}{4} N(4 - N) + \sum_{1 \le k < l \le N} \hat{P}^{\sigma}_{kl} . \qquad (2.13)$$

In the second quantization representation the first term has the same pattern except that the total number of particles N must be replaced by the corresponding operator $\hat{N}$ defined by (2.10).

The operator $\hat{P}_{kl}^{\sigma}$ which interchanges the spin functions of two electrons k and l in the states $\psi_{i\sigma}$ and $\psi_{j\sigma'}$ corresponds to the two-particle operator

$$\sum_{\sigma}\left(\hat{A}_{i\sigma}^{+}\hat{A}_{j\sigma}^{+}\hat{A}_{j\sigma}\hat{A}_{i\sigma}+\hat{A}_{i\sigma}^{+}\hat{A}_{j,-\sigma}^{+}\hat{A}_{j\sigma}\hat{A}_{i,-\sigma}\right). \tag{2.14}$$

Thus, finally

$$\hat{S}^{2}=\frac{1}{4}\hat{N}(4-\hat{N})+\frac{1}{2}\sum_{ij\sigma}\left(\hat{A}_{i\sigma}^{+}\hat{A}_{j\sigma}^{+}\hat{A}_{j\sigma}\hat{A}_{i\sigma}+\hat{A}_{i\sigma}^{+}\hat{A}_{j,-\sigma}^{+}\hat{A}_{j\sigma}\hat{A}_{i,-\sigma}\right). \tag{2.15}$$

Later we shall consider a construction of the eigenvalues of the operators $\hat{S}_z$ and $\hat{S}^2$.

2.3 Hole Formalism

Consider the subset of the spin-orbitals $\{\psi\}_1$, which contains first $2n_F$ one-particle states $\psi_{i\sigma}$ with $i \le n_F$ or one can take n_F pairs of arbitrary spin-orbitals $\psi_{i,+1}$ and $\psi_{i,-1}$ with subsequent renumbering of them, and form a vector

$$\left|\Phi_0\right\rangle=\prod_{i=1}^{n_F}\left(\hat{A}_{i,+1}^{+}\hat{A}_{i,-1}^{+}\right)\left|0\right\rangle. \tag{2.16}$$

This vector corresponds to the Slater determinant built on the spin-orbitals chosen. A determinant built from the same spin-orbitals except $\psi_{j\sigma}$ corresponds to a vector

$$\left|\Phi'\right\rangle=\hat{A}_{j,-\sigma}^{+}\prod_{i=1(i\neq j)}^{n_F}\left(\hat{A}_{i,+1}^{+}\hat{A}_{i,-1}^{+}\right)\left|0\right\rangle. \tag{2.17}$$

Acting on $\left|\Phi'\right\rangle$ by a unit operator

$$\hat{A}_{j\sigma}^{+}\hat{A}_{j\sigma}+\hat{A}_{j\sigma}\hat{A}_{j\sigma}^{+}$$

and using relations (2.1) and (2.5) one obtains

$$\left|\Phi'\right\rangle = \sigma \hat{A}_{j\sigma} \left|\Phi_0\right\rangle . \quad \left(j \le n_F\right) \tag{2.18}$$

This means that action of an operator $\hat{A}_{j\sigma}$ with $j \le n_F$ on the vector $\left|\Phi_0\right\rangle$ leads to the annihilation of a particle in an occupied state $\psi_{j\sigma}$, i.e. to the creation of a hole in this state.

Thus the operators $\hat{A}_{i\sigma}$ and $\hat{A}^+_{i\sigma}$ with $i \le n_F$ can be interpreted as creation and annihilation respectively of the holes in the states of the subset $\{\psi\}_1$. It can be shown that the Slater determinant with u rows changed by other v rows in the second quantization representation corresponds to a vector obtained from $\left|\Phi_0\right\rangle$ by action of u hole creation and v particle creation operators in the corresponding states.

All basis vectors for the CI method can be presented in this way and we shall now describe the corresponding formalism.

Using the anticommutation relations (2.1) and a definition of the vacuum state (2.5) it is easy to see that

$$\hat{A}^+_{i\sigma} \left|\Phi_0\right\rangle = 0, \quad \left\langle\Phi_0\right| \hat{A}_{i\sigma} = 0, \quad \left(i \le n_F\right), \tag{2.19a}$$

$$\hat{A}_{i\sigma} \left|\Phi_0\right\rangle = 0, \quad \left\langle\Phi_0\right| \hat{A}^+_{i\sigma} = 0, \quad \left(i > n_F\right), \tag{2.19b}$$

i.e. $\left|\Phi_0\right\rangle$ is a vacuum state with respect to the creation and annihilation operators of the holes and particles. In the following discussion under the vacuum state we always imply the state $\left|\Phi_0\right\rangle$ and not the initial state $\left|0\right\rangle$.

We shall now introduce the important concept of a *N*-product of the operators $\hat{F}_1, \hat{F}_2, \hat{F}_3, ...$ denoted as $N(\hat{F}_1 \hat{F}_2 \hat{F}_3 \cdots)$. In order to go from the usual product to a normal one we must transpose the operators in such a way that all the hole and particle creation operators are placed to the left of the annihilation operators, and each transposition of a pair of the operators must be followed by change of a sign.

Under the sign of a *N*-product the operators can be arbitrary transposed. The sign depends only on the parity of transposition. An important property of the *N*-product, a consequence of (2.1), is that its average value over the vacuum state is equal to zero

$$\langle \Phi_0 | N(\cdots) | \Phi_0 \rangle = 0 . \tag{2.20a}$$

An obvious exception is the case when under the sign of a *N*-product there is a constant or an expression not having creation or annihilation operators. Then its average over the vacuum state is equal to itself

$$\langle \Phi_0 | N(c) | \Phi_0 \rangle = c . \tag{2.20b}$$

A reduction of operator products to a sum of the *N*-products is extremely useful as shown in calculating the vacuum average of the operator products by expression (2.20). This reduction can be easily performed for a product of two operators using the *N*-products and the anticommutation relations (2.1):

$$\hat{A}\hat{B} = N(\hat{A}\hat{B}) + \overbracket{\hat{A}\hat{B}} . \tag{2.21}$$

The symbol $\overbracket{\hat{A}\hat{B}}$ denotes a *c*-number called a convolution of the operators $\hat{A}$ and $\hat{B}$.

Only the following convolutions of the particle and hole operators are not equal to zero:

$$\overbracket{\hat{A}_{i\sigma}\hat{A}^{+}_{i\sigma}} = 1, \quad \left(i > n_F\right), \tag{2.22a}$$

$$\overbracket{\hat{A}^{+}_{i\sigma}\hat{A}_{i\sigma}} = 1, \quad \left(i \le n_F\right). \tag{2.22b}$$

Thus introducing the population numbers

$$n_i = \begin{Bmatrix} 1, & i \le n_F \\ 0, & i > n_F \end{Bmatrix} \tag{2.23}$$

one obtains for all convolutions

$$\overbrace{\hat{A}_{i\sigma}\hat{A}_{j\sigma'}} = \overbrace{\hat{A}^{+}_{i\sigma}\hat{A}^{+}_{j\sigma'}} = 0\,, \tag{2.24a}$$

$$\overbrace{\hat{A}^{+}_{i\sigma}\hat{A}_{j\sigma'}} = n_i\delta_{ij}\delta_{\sigma\sigma'}\,, \tag{2.24b}$$

$$\overbrace{\hat{A}_{i\sigma}\hat{A}^{+}_{j\sigma'}} = (1-n_i)\delta_{ij}\delta_{\sigma\sigma'}\,. \tag{2.24c}$$

The rules for reduction of the operator product to a sum of the *N*-products in a general case are given by the Wick's theorems [11]. The theorems given in [11] have been formulated by Wick [7] for the chronological products. We give a particular formulation of these theorems for the operators with equal times.

Theorem 1. A product of the creation and annihilation operators is represented by a sum of the normal products with all possible convolutions including a *N*-product without convolutions. The sign of each term is determined by a number of the operator transpositions needed that the convoluting operators are grouped together:

$$\begin{aligned} \hat{F}_1\hat{F}_2\hat{F}_3\cdots\hat{F}_n &= N(\hat{F}_1\hat{F}_2\hat{F}_3\cdots\hat{F}_n) + \overbrace{\hat{F}_1\hat{F}_2}\,N(\hat{F}_3\hat{F}_4\hat{F}_5\cdots\hat{F}_n) - \\ &- \overbrace{\hat{F}_1\hat{F}_3}\,N(\hat{F}_2\hat{F}_4\hat{F}_5\cdots\hat{F}_n) + \ldots + \overbrace{\hat{F}_1\hat{F}_2}\,\overbrace{\hat{F}_3\hat{F}_4}\,N(\hat{F}_5\hat{F}_6\hat{F}_7\cdots\hat{F}_n) + \ldots \end{aligned}$$

Theorem 2. If some operators in the product to be reduced stand from the beginning under the sign of the *N*-product then the reduction is made in the same way except that the convolutions must be omitted for those operators which from the beginning were standing under the sign of the same *N*-product.

2.4 Expansion of the Physical Value Operators over the N-products

For a one-particle operator using (2.21) and (2.24) one obtains from (2.11)

$$\hat{Q} \equiv \sum_{ij\sigma\sigma'} N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{j\sigma'}\right)\langle\psi_{i\sigma}|\hat{Q}|\psi_{j\sigma'}\rangle + \sum_{i\sigma} n_i \langle\psi_{i\sigma}|\hat{Q}|\psi_{i\sigma}\rangle . \qquad (2.25)$$

In particular, if an operator $\hat{Q}$ does not act on the spin variables, then

$$\hat{Q} = \sum_{ij\sigma} N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{j\sigma}\right)Q_{ij} + 2\sum_{i} n_i Q_{ii} , \qquad (2.26)$$

where

$$Q_{ij} = \langle\varphi_i|\hat{Q}|\varphi_j\rangle . \qquad (2.27)$$

One obtains in the same way from (2.12)

$$\hat{S}_z = \frac{1}{2}\sum_{i\sigma} \sigma N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{i\sigma}\right) . \qquad (2.28)$$

The number-of-paticles operator (2.10) becomes

$$\hat{N} = \sum_{i\sigma} N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{i\sigma}\right) + 2n_F . \qquad (2.29)$$

Now we shall transform the Hamiltonian (2.2). The first sum in (2.2) is transformed according to (2.26) with $\hat{Q} = \hat{h}$. In order to transform a sum corresponding to the electron interaction we use the first Wick theorem. Its application to a product of four operators gives

$$
\begin{aligned}
\hat{A}^{+}_{i\sigma}\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}\hat{A}_{k\sigma} = {}& N\left(\hat{A}^{+}_{i\sigma}\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}\hat{A}_{k\sigma}\right) + \overbrace{\hat{A}^{+}_{i\sigma}\hat{A}_{k\sigma}}\, N\left(\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}\right) + \overbrace{\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}}\, N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{k\sigma}\right) - \\
& - \overbrace{\hat{A}^{+}_{j\sigma'}\hat{A}_{k\sigma}}\, N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{l\sigma'}\right) - \overbrace{\hat{A}^{+}_{i\sigma'}\hat{A}_{l\sigma}}\, N\left(\hat{A}^{+}_{j\sigma'}\hat{A}_{k\sigma}\right) + \overbrace{\hat{A}^{+}_{i\sigma}\hat{A}_{k\sigma}}\,\overbrace{\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}} - \overbrace{\hat{A}^{+}_{i\sigma}\hat{A}_{l\sigma'}}\,\overbrace{\hat{A}^{+}_{j\sigma}\hat{A}_{k\sigma'}}\,,
\end{aligned}
\tag{2.30}
$$

where only those terms are written down which can have non-zero convolutions. Putting this expansion into (2.2) and substituting all convolutions by their values according to (2.24), after the necessary summations one obtains

$$
\hat{H} = E_0 + \sum_{ij\sigma} F_{ij} N\left(\hat{A}^{+}_{i\sigma}\hat{A}_{j\sigma}\right) + \frac{1}{2}\sum_{ijkl\sigma\sigma'} (ij\,|\,kl) N\left(\hat{A}^{+}_{i\sigma}\hat{A}^{+}_{j\sigma'}\hat{A}_{l\sigma'}\hat{A}_{k\sigma}\right), \tag{2.31}
$$

where

$$
E_0 = 2\sum_{i} n_i h_{ii} + \sum_{ij} n_i n_j \left[2\left(ij\,|\,ij\right) - (ij\,|\,ji)\right] \tag{2.32}
$$

and

$$
F_{ij} = h_{ij} + \sum_{k} n_k \left[2\left(ik\,|\,jk\right) - \left(ik\,|\,kj\right)\right]. \tag{2.33}
$$

Expression (2.32) is the well known equation for the energy in the Hartree – Fock approximation and F_{ij} are the matrix elements

$$
F_{ij} = \left\langle \varphi_i \middle| \hat{F} \middle| \varphi_j \right\rangle
$$

of the Fock operator built on the orbitals $\varphi_1, \varphi_2, \varphi_3, \ldots, \varphi_{n_F}$. If these orbitals are eigenfunctions of the SCF Fock operator with eigenvalues ε_i then

$$
F_{ij} = \varepsilon_i \delta_{ij}
$$

and the Hamiltonian (2.31) becomes

$$\hat{H} = E_0 + \sum_{i\sigma} \varepsilon_i N\left(\hat{A}^+_{i\sigma}\hat{A}_{i\sigma}\right) + \frac{1}{2}\sum_{ijkl\sigma\sigma'} (ij\,|\,kl) N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{j\sigma'}\hat{A}_{l\sigma'}\hat{A}_{k\sigma}\right). \tag{2.34}$$

This particular expression for the Hamiltonian is applicable only under the conditions mentioned. The general expression (2.31), however, is valid for an arbitrary orthonormal set of orbitals.

Following the same procedure one can obtain an expression for the operator $\hat{S}^2$ given by (2.15). We present the final result

$$\begin{aligned}\hat{S}^2 = {} & \frac{3}{4}\sum_{i\sigma}(1-2n_i)N(\hat{A}^+_{i\sigma}\hat{A}_{i\sigma}) + \frac{1}{4}\sum_{ij\sigma} N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{j\sigma}\hat{A}_{j\sigma}\hat{A}_{i\sigma}\right) - \frac{1}{4}\sum_{ij\sigma(i\neq j)} N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{i,-\sigma}\hat{A}_{j,-\sigma}\hat{A}_{i\sigma}\right) - \\ & - \frac{3}{4}\sum_{i\sigma} N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{i,-\sigma}\hat{A}_{i,-\sigma}\hat{A}_{i\sigma}\right) + \frac{1}{2}\sum_{ij\sigma(i\neq j)} N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{j,-\sigma}\hat{A}_{j\sigma}\hat{A}_{i,-\sigma}\right).\end{aligned} \tag{2.35}$$

The fourth sum in (2.35) contains terms with $i = j$ from the third and fifth sums.

Having derived expressions for the operators $\hat{S}_z$ and $\hat{S}^2$ in an appropriate form we can construct the basis vectors for the CI method which are eigenfunctions of these operators. First we note that any vector obtained as a result of the action of N_p particle and N_h hole creation operators on the vacuum state $|\Phi_0\rangle$ is an eigenvector of the operator $\hat{N}$ with an eigenvalue $N_p - N_h + 2n_F$ which is equal to the total number of particles.

By fixing this number we need consider only vectors with a definite value of the difference $N_p - N_h$. In most cases the vacuum state can be chosen in such a way that N_p is equal to N_h (the ground state of a molecule with closed shell) or differs from N_h by one (a radical).

Next we choose the electronic configuration. Let us set up the electronic configuration by selecting the orbitals corresponding to N_p particles and N_h holes irrespective of their spins. We shall denote it as $(k_1k_2k_3...k_{N_h}, m_1m_2m_3...m_{N_p})$ where k_i corresponds to the hole orbitals, and m_i numerate the particle orbitals. These numbers are supposed to be arranged in a non-decreasing order (naturally $k_{N_h} < n_F$, $m_1 > n_F$). Furthermore, according to the Pauli principle each number cannot occur more than once.

Now for the configuration above $(k_1k_2..., m_1m_2...)$ we construct all possible vectors as

$$\hat{A}_{k_1\sigma_1}\hat{A}_{k_2\sigma_2}\cdots\hat{A}^{+}_{m_1\sigma_1'}\hat{A}^{+}_{m_2\sigma_2'}\cdots\left|\Phi_0\right\rangle, \tag{2.36}$$

which in the following discussion are called the primitive vectors. Each of the spin indices $\sigma_1,\sigma_2,...,\sigma_1',\sigma_2',...$ independently assumes values +1 and –1 except those cases when $k_i = k_i + 1$ and $m_i = m_{i+1}$ for which necessary $\sigma_i = -\sigma_{i+1} = 1$ and $\sigma_i' = -\sigma_{i+1}' = 1$. Under these conditions the primitive vectors constructed form an orthonormal system. Each of them is an eigenvector of the operator $\hat{S}_z$ with the eigenvalue

$$M_S = \frac{1}{2}\left[\left(N_p^{+} - N_p^{-}\right) - \left(N_h^{+} - N_h^{-}\right)\right],$$

where $N_p^{+}, N_p^{-}, N_h^{+}, N_h^{-}$ is the number of particle and hole operators with the spin +1 and –1 correspondingly.

To determine the necessary basis vectors one selects for each configuration all primitive vectors (2.36) with a given value of the difference $\left(N_p^{+} - N_p^{-}\right) - \left(N_h^{+} - N_h^{-}\right)$, construct a matrix of the operator $\hat{S}^2$ for them, and diagonalizes it. The result of the application of the operator $\hat{S}^2$ on the primitive vector represented at first sight as a cumbersome expression (2.35) is obtained by the following rules.

Rule 1. The action of the first four sums in (2.35) on a vector (2.36) reduces to a multiplication of it by a constant. Its value is equal to the value of M_S^2 plus half the sum of N_p and N_h minus the number of orbitals occupied in pairs by particles and holes with opposite spins. All diagonal elements of the matrix of the operator $\hat{S}^2$ will be equal to the constant found so far.

Rule 2. The remaining part of the expression for $\hat{S}^2$ acts on a vector (2.36) converting it to a sum of the vectors orthogonal to (2.36). Each of them differs from the initial vector by change on opposite the spin indices of two particle-particle or hole-hole operators with different spins or the particle-hole operators with equal spins. In the later case a vector enters a sum with a minus sign. It is necessary to consider all mentioned pairs of operators used to construct an initial vector except those operators which correspond in pairs to the same orbitals.

2.5 General Approach to Calculation of the Matrix Elements

Previous treatment shows that the basis vectors are linear combinations of the primitive vectors, and the operators of the important physical values reduce to three basic types:

$$\hat{\Omega}_0 = N(c)\,, \tag{2.37a}$$

$$\hat{\Omega}_1 = \sum_{ij\sigma} Q_{ij,\sigma} N\left(\hat{A}^+_{i\sigma}\hat{A}_{j\sigma}\right), \tag{2.37b}$$

$$\hat{\Omega}_2 = \frac{1}{2}\sum_{ijkl\sigma\sigma'} (ij\,|\,kl) N\left(\hat{A}^+_{i\sigma}\hat{A}^+_{j\sigma'}\hat{A}_{l\sigma'}\hat{A}_{k\sigma}\right). \tag{2.37c}$$

Take two primitive vectors corresponding to the same or to different configurations

$$\left|\Phi_1\right\rangle = \hat{A}_{k_1\sigma_1}\hat{A}_{k_2\sigma_2}\cdots\hat{A}^+_{m_1\sigma'_1}\hat{A}^+_{m_2\sigma'_2}\cdots\left|\Phi_0\right\rangle, \tag{2.38a}$$

$$\left|\Phi_2\right\rangle = \hat{A}_{l_1\tau_1}\hat{A}_{l_2\tau_2}\cdots\hat{A}^+_{n_1\tau'_1}\hat{A}^+_{n_2\tau'_2}\cdots\left|\Phi_0\right\rangle. \tag{2.38b}$$

We shall calculate for them the matrix elements of each of the operators (2.37). Denoting

$$\hat{R}_1 = \hat{A}_{k_1\sigma_1}\hat{A}_{k_2\sigma_2}\cdots\hat{A}^+_{m_1\sigma'_1}\hat{A}^+_{m_2\sigma'_2}\cdots, \tag{2.39a}$$

$$\hat{R}^+_1 = \cdots\hat{A}_{m_2\sigma'_2}\hat{A}_{m_1\sigma'_1}\cdots\hat{A}^+_{k_2\sigma_2}\hat{A}^+_{k_1\sigma_1}\,, \tag{2.39b}$$

$$\hat{R}_2 = A_{l_1\tau_1}A_{l_2\tau_2}\cdots A^+_{n_1\tau'_1}A^+_{n_2\tau'_2}\cdots, \tag{2.39c}$$

the matrix element of an operator $\hat{\Omega}$, any of the operators (2.37), may be considered as the vacuum average

$$\langle\Phi_1|\hat{\Omega}|\Phi_2\rangle = \langle\Phi_0|\hat{R}_1^+\hat{\Omega}\hat{R}_2|\Phi_0\rangle\,. \tag{2.40}$$

To calculate (2.40), the product $\hat{R}_1^+\hat{\Omega}\hat{R}_2$ must be reduced applying the Wick's theorems to the sum of the *N*-products. As a result of the averaging according to (2.20) only those terms remain which are *c*-numbers, *i.e.* those terms in which all operators in $\hat{R}_1^+\hat{\Omega}\hat{R}_2$ enter the convolutions.

The advantage of the presentations of the physical value operators as a sum of *N*-products is now evident. Since $\hat{R}_1^+$ is a product of the particle and hole annihilation operators only, and $\hat{R}_2$ – of the creation operators only, then $\hat{R}_1^+ = N(\hat{R}_1^+)$, $\hat{R}_2 = N(\hat{R}_2)$ and according to the second Wick's theorem one must consider only the convolutions between the operators $\hat{R}_1^+$, $\hat{\Omega}$, and $\hat{R}_2$.

After this preliminary remark we continue the determination of the value of the matrix elements. First we find the maximum number of convolutions which can be constructed between the operators from $\hat{R}_1^+$ and $\hat{R}_2$. This number is equal to the number of particles and hole operators in $\hat{R}_1$ which are repeated in $\hat{R}_2$. The operators in $\hat{R}_1$ as well as in $\hat{R}_2$ may be transposed in an arbitrary way multiplying the value of the matrix element by $(-1)^{p_1}$, where p_1 is the total number of transpositions.

For this reason it is convenient to order the operators in $\hat{R}_1$ and $\hat{R}_2$ first, transposing them in such a way that the repeating operators are placed in $\hat{R}_1$ and $\hat{R}_2$ in the same order to the right of the non-repeating operators.

We shall assume in the following that this ordering is performed. The total number of non-repeating operators in $\hat{R}_1$ and $\hat{R}_2$ will be denoted q. Because each of these q operators may be convoluted with one of the operators from $\hat{\Omega}$ one can state *a priori* that the matrix element

$$\langle\Phi_0|\hat{R}_1^+\hat{\Omega}\hat{R}_2|\Phi_0\rangle$$

will not be equal to zero only for $q = 0$ if $\hat{\Omega} = \hat{\Omega}_0$, for $q = 0,2$ if $\hat{\Omega} = \hat{\Omega}_1$, and for $q = 0,2,4$ if $\hat{\Omega} = \hat{\Omega}_2$.

We shall consider each of these cases separately. In cases when the total number of the operators in $\hat{R}_1$ and $\hat{R}_2$ is less than 2 for $\hat{\Omega} = \hat{\Omega}_1$ or less than 4 for $\hat{\Omega} = \hat{\Omega}_2$ the value of the corresponding matrix elements is obviously equal to zero.

Case 1: $\hat{\Omega} = \hat{\Omega}_0$, $q = 0$. The convolution which gives a non-zero result can be done in a single way convoluting in pairs the repeating operators. When $\hat{R}_1$ and $\hat{R}_2$ are correctly ordered there is always an even number of other operators between the convoluting operators. Thus, the number of transpositions required by the first Wick theorem is also even and each convolution according to (2.24) is equal to unity. Finally the value of the matrix element will be equal to

$$\langle \Phi_1 | \hat{\Omega}_0 | \Phi_2 \rangle = (-1)^{p_1} c. \tag{2.41}$$

Case 2: $\hat{\Omega} = \hat{\Omega}_1$, $q = 0$. In this case the vacuum average is equal to the sum of the terms each of which is the result of a convolution of two operators from $\hat{\Omega}_1$ with two equal operators from $\hat{R}_1$ and $\hat{R}_2$. The other operators repeating in $\hat{R}_1$ and $\hat{R}_2$, if there are any, convolute between them in pairs. The final result is

$$\langle \Phi_1 | \hat{\Omega}_1 | \Phi_2 \rangle = (-1)^{p_1} \sum_{i\sigma} Q_{ii,\sigma} \left(1 - 2n_i\right), \tag{2.42}$$

where a pair of indices i,σ covers the interval met in $\hat{R}_1$.

Case 3: $\hat{\Omega} = \hat{\Omega}_1$, $q = 2$. The single term in the expansion of $\hat{R}_1^{+}\hat{\Omega}\hat{R}_2$ over the *N*-products the vacuum average of which may be different from zero is obtained in the following way. All operators from $\hat{R}_1$ repeating in $\hat{R}_2$ convolute with the corresponding operators from $\hat{R}_1^{+}$. Two non-repeating operators convolute with the operators from $\hat{\Omega}_1$.

The results is

$$\langle \Phi_1 | \hat{\Omega}_1 | \Phi_2 \rangle = (-1)^{p_1 + p_2} \delta_{\sigma_1\sigma_2} Q_{i_1 i_2,\sigma_1}, \tag{2.43}$$

where p_2 is the number of transpositions necessary to place in the product $\hat{R}_1\hat{R}_2^+$ the non-repeating operator with a cross at the left of the non-repeating operator without a cross (2. p_2 is equal to 1 or 0), and a pair of indices i_1,σ_1 runs over the indices of the non-repeating operator with a cross, and a pair i_2,σ_2 – without a cross in the product $\hat{R}_1\hat{R}_2^+$.

Case 4: $\hat{\Omega}=\hat{\Omega}_2,\ q=0$. For each pair of operators from $\hat{R}_2$ in the matrix element expression for this case there are possible four terms identical in pairs obtained by convoluting these operators and the corresponding pair of operators from $\hat{R}_1^+$ with four operators from $\hat{\Omega}_2$

$$\langle\Phi_1|\hat{\Omega}_2|\Phi_2\rangle=(-1)^{p_1}\sum_{ij\sigma\sigma'}\left[(ij\,|\,ij)-\delta_{\sigma\sigma'}(ij\,|\,ji)\right](1-2n_i)\left(1-2n_j\right), \qquad (2.44)$$

where a pair of indices i,σ runs in the interval met in the operators from $\hat{R}_1$ and a pair j,σ' covers all values of indices of the operators from $\hat{R}_1$ placed to the right of the operator with indices i,σ.

Case 5: $\hat{\Omega}=\hat{\Omega}_2,\ q=2$. In the expansion of each of the repeating operators in $\hat{R}_2$ four terms identical in pairs may not be equal to zero. They are obtained by the convoluting with the operators from $\hat{\Omega}_2$ of two non-repeating operators, and one of the operators in $\hat{R}_2$ repeating in $\hat{R}_1$, and the corresponding operator from $\hat{R}_1^+$.

The final result is

$$\langle\Phi_1|\hat{\Omega}_2|\Phi_2\rangle=(-1)^{p_1+p_2}\delta_{\sigma_1\sigma_2}\sum_{i\sigma}(1-2n_i)\left[(ii_1\,|\,ii_2)-\delta_{\sigma\sigma_1}(ii_1\,|\,i_2i)\right], \qquad (2.45)$$

where a pair of indices i,σ covers all values met in the repeating operators, and a value of p_2 and indices $i_1,i_2,\sigma_1,\sigma_2$ are defined as in case 3.

Case 6: $\hat{\Omega}=\hat{\Omega}_2,\ q=4$. In this last case there may not be equal to zero the four in pairs identical terms obtained by convoluting four non-repeating operators from $\hat{R}_1^+\hat{R}_2$ with four operators from $\hat{\Omega}_2$. The result can be obtained in the following way.

Let us write all non-repeating operators in the same order as they are placed in the product $\hat{R}_1 \hat{R}_2^+$ and order them in such a way that the cross operators stand to the left of the non-cross operators. Let p_3 be the number of transpositions made in order to obtain standard order

$$\hat{A}^+_{i_1\sigma_1} \hat{A}^+_{i_2\sigma_2} \hat{A}_{i_3\sigma_3} \hat{A}_{i_4\sigma_4} .$$

Then the value of the matrix element is

$$\langle \Phi_1 | \hat{\Omega}_2 | \Phi_2 \rangle = (-1)^{p_1+p_2} \left[\delta_{\sigma_1\sigma_4} \delta_{\sigma_2\sigma_3} \left(i_1 i_2 \,|\, i_4 i_3 \right) - \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \left(i_1 i_2 \,|\, i_3 i_4 \right) \right]. \quad (2.46)$$

2.6 Matrix Elements of the Physical Value Operators for Molecules and Radicals with Account of Singly and Doubly Excited Configurations as an Example of the General Approach

Analytical expressions for the matrix elements of the operators are useful only for simple configurations and for the derivation of various general statements. For complex configurations it is expedient to adopt a calculation scheme given above and suitable for programming. Now we give for the case of the singly and doubly excited configurations for molecules and radicals some basis vectors which will be useful in further applications [12]. They are given in a final form, and some of them are compared with the expressions available in the literature. When deriving analytical expressions for the matrix elements we did not assume any restrictions on an orthonormal orbital set used for the construction of the configurations. We also consider some general expressions for the SCF orbitals and will show that in the case of radicals some Hamiltonian matrix elements between the ground configuration and the singly excited configurations vanish. Finally, we shall give formulae for the calculation of some molecular and radical properties by the CI method such as electronic density of atoms, bond orders, transition moments, and spin distribution.

2.6.1 Basis Vectors

Consider the singly excited configurations (k,m) of a molecule with closed shells in the ground state. In this case $N_p = N_h = 1$ and four primitive vectors are possible:

$$|\Phi_1\rangle = \hat{A}_{k+}\hat{A}^{+}_{m+}|\Phi_0\rangle \ , \ |\Phi_3\rangle = \hat{A}_{k-}\hat{A}^{+}_{m+}|\Phi_0\rangle , \tag{2.47a}$$

$$|\Phi_2\rangle = \hat{A}_{k-}\hat{A}^{+}_{m-}|\Phi_0\rangle , \ |\Phi_4\rangle = \hat{A}_{k+}\hat{A}^{+}_{m-}|\Phi_0\rangle . \tag{2.47b}$$

Using the rules of p.4 above one obtains

$$\hat{S}^2|\Phi_1\rangle = |\Phi_1\rangle - |\Phi_2\rangle , \ \hat{S}^2|\Phi_3\rangle = 2|\Phi_3\rangle , \tag{2.48a}$$

$$\hat{S}^2|\Phi_2\rangle = -|\Phi_1\rangle + |\Phi_2\rangle , \ \hat{S}^2|\Phi_4\rangle = 2|\Phi_4\rangle . \tag{2.48b}$$

As expected, the matrix of the operator $\hat{S}^2$ reduces to one two-row and two one-row matrices. By diagonalizing the former one obtains the following normalized basis vectors

$$|{}^1\Psi_1\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_1\rangle + |\Phi_2\rangle\right), \quad M_S = 0, \quad S = 0, \tag{2.49a}$$

$$|{}^3\Psi_1\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_1\rangle - |\Phi_2\rangle\right), \quad M_S = 0, \quad S = 1, \tag{2.49b}$$

$$|{}^3\Psi_2\rangle = |\Phi_3\rangle, \qquad M_S = 1, \quad S = 1, \tag{2.49c}$$

$$|{}^3\Psi_3\rangle = |\Phi_4\rangle, \qquad M_S = -1, \quad S = 1. \tag{2.49d}$$

There are unusual signs in the first two vectors.

In the case of a radical the vacuum state $|\Phi_0\rangle$ is chosen as the closed shell of its ground state. Then one kind of the basis vectors is obviously

$$|{}^2\Psi_1\rangle = \hat{A}^{+}_{m+}|\Phi_0\rangle . \tag{2.50}$$

Now we consider the basis vectors for the configuration (k,mn) of a radical limiting of ourselves to the vectors with $M_S = 1/2$. The corresponding primitive vectors are

$$\left|\Phi_5\right\rangle = \hat{A}_{k-}\hat{A}^+_{m+}\hat{A}^+_{n-}\left|\Phi_0\right\rangle, \qquad (2.51a)$$

$$\left|\Phi_6\right\rangle = \hat{A}_{k+}\hat{A}^+_{m+}\hat{A}^+_{n+}\left|\Phi_0\right\rangle, \qquad (2.51b)$$

$$\left|\Phi_7\right\rangle = \hat{A}_{k-}\hat{A}^+_{m-}\hat{A}^+_{n+}\left|\Phi_0\right\rangle. \qquad (2.51c)$$

When $n = m$, the vector $\left|\Phi_6\right\rangle$ vanishes, and the vector $\left|\Phi_5\right\rangle$ differs from $\left|\Phi_7\right\rangle$ only by sign and becomes another basis vector

$$\left|{}^2\Psi_2\right\rangle = \hat{A}_{k-}\hat{A}^+_{m+}\hat{A}^+_{m-}\left|\Phi_0\right\rangle. \qquad (2.52)$$

Let be $n \neq m$. Writing

$$\hat{S}^2\left|\Phi_i\right\rangle = \sum_{j=5}^{7} S^2_{ij}\left|\Phi_j\right\rangle, \qquad (2.53)$$

and using the rules of $\#4$ one obtains a matrix

$$S^2 = \begin{bmatrix} 7/4 & -1 & 1 \\ -1 & 7/4 & -1 \\ 1 & -1 & 7/4 \end{bmatrix}. \qquad (2.54)$$

Diagonalizing this matrix we obtain eigenvector (2.1, –1, 1) corresponding to an eigenvalue 5/4 and two vectors (2.1, –1, –2) and (2.1, 1, 0) for degenerated eigenvalue 3/4 . Therefore the normalized doublet and quartet basis vectors are, respectively,

$$\left|{}^2\Psi_3\right\rangle = \frac{1}{\sqrt{6}}\left(\left|\Phi_5\right\rangle - \left|\Phi_6\right\rangle - 2\left|\Phi_7\right\rangle\right), \qquad (2.55a)$$

$$\left|{}^2\Psi_4\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\Phi_5\right\rangle + \left|\Phi_6\right\rangle\right) \tag{2.55b}$$

and

$$\left|{}^4\Psi_1\right\rangle = \frac{1}{\sqrt{3}}\left(\left|\Phi_5\right\rangle - \left|\Phi_6\right\rangle + \left|\Phi_7\right\rangle\right). \tag{2.56}$$

The doublet basis vectors are determined up to a unitary transformation. We have chosen the vectors (2.55) to correspond to those found in the literature.

2.6.2 Elements of the CI matrix

The final expressions for the matrix elements of the Hamiltonian (2.31) obtained by using the results of p. 2.5 above are now given.

Molecule

$$\left\langle\Phi_0\right|\hat{H}\left|{}^{1,3}\Phi_1\right\rangle = -f\sqrt{2}F_{km}\,, \tag{2.57}$$

$$\left\langle{}^{1,3}\Phi_1'\right|\hat{H}\left|{}^{1,3}\Phi_1\right\rangle = \delta_{kk'}\delta_{mm'}E_0 + \delta_{kk'}F_{m'm} - \delta_{mm'}F_{kk'} + 2f\,(km'\,|\,mk') - (km'\,|\,k'm)\,, \tag{2.58}$$

where

$$f = \begin{cases} 0 & for \quad S = 1, \\ 1 & for \quad S = 0. \end{cases}$$

Here and in the following expressions the primes are used for numbers of those particles and holes which constitute the basis vectors placed at the left of the Hamiltonian.

Radical

$$\left\langle{}^2\Phi_1'\right|\hat{H}\left|{}^2\Phi_1\right\rangle = \delta_{mm'}E_0 + F_{m'm}\,, \tag{2.59}$$

$$\begin{aligned}\left\langle{}^2\Phi_2'\right|\hat{H}\left|{}^2\Phi_2\right\rangle = \delta_{kk'}\delta_{mm'}E_0 + \delta_{mm'}(2\delta_{kk'}F_{m'm} - F_{kk'}) + \delta_{kk'}(m'm'\,|\,mm) + \\ + \delta_{mm'}[(km'\,|\,mk') - 2(km'\,|\,k'm)],\end{aligned} \tag{2.60}$$

$$\begin{aligned}\left\langle {}^2\Phi_3'\middle|\hat{H}\middle|{}^2\Phi_3\right\rangle = {}&\delta_{kk'}(\delta_{mm'}\delta_{nn'}-\delta_{mn'}\delta_{nm'})E_0+\tfrac{1}{2}\{\delta_{kk'}(2\delta_{mm'}F_{n'n}+2\delta_{nn'}F_{m'm}+\delta_{mn'}F_{m'n}+\delta_{nm'}F_{n'm})-\\&-F_{kk'}(2\delta_{mm'}\delta_{nn'}+\delta_{mn'}\delta_{nm'})+\delta_{kk'}[2(m'n'\,|\,mn)+(m'n'\,|\,nm)]-2\delta_{mm'}(kn'\,|\,k'n)+\\&+\delta_{nn'}[3(m'k\,|\,k'm)-2(m'k\,|\,mk')]-\delta_{mn'}(m'k\,|\,nk')-\delta_{nm'}(n'k\,|\,mk')\},\end{aligned}\tag{2.61}$$

$$\begin{aligned}\left\langle {}^2\Phi_4'\middle|\hat{H}\middle|{}^2\Phi_4\right\rangle = {}&\delta_{kk'}(\delta_{mm'}\delta_{nn'}-\delta_{mn'}\delta_{nm'})E_0+\tfrac{1}{2}\{\delta_{kk'}(2\delta_{mm'}F_{n'n}+2\delta_{nn'}F_{m'm}-\delta_{mn'}F_{m'n}-\delta_{nm'}F_{n'm})-\\&-F_{kk'}(2\delta_{mm'}\delta_{nn'}-\delta_{mn'}\delta_{nm'})+\delta_{kk'}[2(m'n'\,|\,mn)-(m'n'\,|\,nm)]+2\delta_{mm'}[2(kn'\,|\,nk')-\\&-(kn'\,|\,k'n)]+\delta_{nn'}[(m'k\,|\,k'm)-2(m'k\,|\,mk')]+\delta_{mn'}[(m'k\,|\,nk')-2(m'k\,|\,k'n)]+\\&+\delta_{nm'}[(n'k\,|\,mk')-2(n'k\,|\,k'm)]\},\end{aligned}\tag{2.62}$$

$$\left\langle {}^2\Phi_1'\middle|\hat{H}\middle|{}^2\Phi_2\right\rangle=\delta_{mm'}F_{km}+(km'\,|\,mm),\tag{2.63}$$

$$\left\langle {}^2\Phi_1'\middle|\hat{H}\middle|{}^2\Phi_3\right\rangle=\sqrt{\frac{3}{2}}\delta_{nm'}F_{km}+(km'\,|\,mn),\tag{2.64}$$

$$\left\langle {}^2\Phi_1'\middle|\hat{H}\middle|{}^2\Phi_4\right\rangle=\frac{1}{\sqrt{2}}[2\delta_{mm'}F_{kn}-\delta_{nm'}F_{km}+2(km'\,|\,nm)-(km'\,|\,mn)],\tag{2.65}$$

$$\left\langle {}^2\Phi_2'\middle|\hat{H}\middle|{}^2\Phi_3\right\rangle=\frac{1}{\sqrt{6}}\{\delta_{kk'}[(m'm'\,|\,mn)-(m'm'\,|\,nm)]+2\delta_{mm'}(km'\,|\,nk')-2\delta_{nm'}(m'k\,|\,k'm)\},\tag{2.66}$$

$$\begin{aligned}\left\langle {}^2\Phi_2'\middle|\hat{H}\middle|{}^2\Phi_4\right\rangle={}&\frac{1}{\sqrt{2}}\{\delta_{kk'}(\delta_{mm'}F_{m'n}+\delta_{nm'}F_{m'm})-\delta_{nm'}\delta_{mm'}F_{kk'}+\delta_{kk'}(m'm'\,|\,mn)+\\&+\delta_{mm'}[2(km'\,|\,nk')-(km'\,|\,k'n)]-\delta_{nm'}[(m'k\,|\,k'm)+(m'k\,|\,mk')]\},\end{aligned}\tag{2.67}$$

$$\begin{aligned}\left\langle {}^2\Phi_3'\middle|\hat{H}\middle|{}^2\Phi_4\right\rangle={}&\frac{1}{\sqrt{3}}\{\delta_{kk'}(\delta_{mm'}F_{n'n}+\delta_{nn'}F_{m'm}-\delta_{mn'}F_{m'n}-\delta_{nm'}F_{n'm})-F_{kk'}(\delta_{mm'}\delta_{nn'}-\delta_{mn'}\delta_{nm'})+\\&+\delta_{kk'}[(m'n'\,|\,mn)-(m'n'\,|\,nm)]+\delta_{mm'}[2(kn'\,|\,nk')-(kn'\,|\,k'n)]+\\&+\delta_{nn'}[(m'k\,|\,k'm)-(m'k\,|\,mk')]+\delta_{mn'}[(m'k\,|\,nk')-2(m'k\,|\,k'n)]+\\&+\delta_{nm'}[(n'k\,|\,mk')-(n'k\,|\,k'm)]\}.\end{aligned}\tag{2.68}$$

Formula (2.59) is well known, *e.g.* in [13, 14]. Particular cases of some of the general expressions above can be found in the quantum chemistry literature, *e.g.* formula (2.60) for $k' = k, m' = m$ and (2.62) for $k' = k, m' = m, n' = n$ in [13], formula (2.63) for $m' \neq m$ in [13] and for $m' = m$ in [14], formula (2.64) for $m' = m$ in [14].

2.6.3 The Brillouin Theorem and its Analog for Radicals

The orthonormal orbitals for which the first variation of energy E_0 of the vacuum state $|\Phi_0\rangle$ vanishes according to [15] satisfy the operator equation

$$\hat{F}\hat{P}_1 - \hat{P}_1\hat{F} = 0, \tag{2.69}$$

where $\hat{F}$ is the Fock operator, and $\hat{P}_1$ is the Fock – Dirac density operator

$$\hat{P}_1 = \sum_{l=1}^{n_F} |\varphi_l\rangle\langle\varphi_l|. \tag{2.70}$$

Calculating the matrix element of (2.69) over the orbitals φ_k and φ_m and using projection properties of the operator $\hat{P}_1$ one obtains from (2.57) if initial orbitals satisfy equation (2.69) that

$$\langle\Phi_0|\hat{H}|{}^1\Phi_1\rangle = 0. \tag{2.71}$$

The conditions used in deriving (2.71) are more comprehensive than the conditions of the well known Brillouin theorem [16, 17]. The content of this theorem is expressed by (2.71) if configurations are built on the SCF eigenfunctions of the operator $\hat{F}$.

In the case of a radical the orbitals for which the first variation of the energy of the configuration $(-,m)$ vanishes satisfy the operator equation [18]

$$\hat{F}_1\hat{P}_1 - \hat{P}_1\hat{F}_1 + \hat{F}_2\hat{P}_2 - \hat{P}_2\hat{F}_2 = 0, \tag{2.72}$$

where $\hat{P}_1$ is defined by (2.70), $\hat{P}_2$ is a projection operator for the orbital φ_m, and the operators $\hat{F}_1$ and $\hat{F}_2$ for a semi-open shell are determined as

$$\hat{F}_1 = \hat{F} + \hat{J}_0 - \frac{1}{2}\hat{K}_0 , \tag{2.73}$$

$$\hat{F}_2 = \frac{1}{2}\hat{F} + \hat{J}_0 - \hat{K}_0 \tag{2.74}$$

with the Fock operator $\hat{F}$ built on the vacuum orbitals, and Coulomb $\hat{J}_0$ and exchange $\hat{K}_0$ operators are built on the orbital φ_m .

Let us write down the expressions for the matrix elements (2.59) for $m' \neq m$ and (2.63), (2.65) for $m' \neq m, n \neq m$

$$\left\langle {}^2\Phi_1 \middle| \hat{H} \middle| {}^2\Phi_1' \right\rangle = F_{mm'} , \tag{2.75}$$

$$\left\langle {}^2\Phi_1 \middle| \hat{H} \middle| {}^2\Phi_2 \right\rangle = F_{km} + (\hat{J}_0)_{km} , \tag{2.76}$$

$$\left\langle {}^2\Phi_1 \middle| \hat{H} \middle| {}^2\Phi_4 \right\rangle = \sqrt{2}[F_{kn} + (\hat{J}_0)_{kn} - \frac{1}{2}(\hat{K}_0)_{kn}] , \tag{2.77}$$

where the last two matrix elements are expressed over the matrix elements of the operators $\hat{J}_0$ and $\hat{K}_0$ on the orbitals φ_i .

Using projection properties of the operators $\hat{P}_1$ and $\hat{P}_2$

$$\hat{P}_1|\varphi_k\rangle = |\varphi_k\rangle, \quad \hat{P}_1|\varphi_m\rangle = \hat{P}_1|\varphi_{m'}\rangle = \hat{P}_1|\varphi_n\rangle = 0 , \tag{2.78a}$$

$$\hat{P}_2|\varphi_m\rangle = |\varphi_m\rangle, \hat{P}_2|\varphi_k\rangle = \hat{P}_2|\varphi_{m'}\rangle = \hat{P}_2|\varphi_n\rangle = 0 \tag{2.78b}$$

from equation (2.72) one obtains

$$\begin{aligned} &\langle \varphi_m | \hat{F}_2 | \varphi_{m'} \rangle = 0, \\ &\langle \varphi_k | \hat{F}_1 - \hat{F}_2 | \varphi_m \rangle = 0, \\ &\langle \varphi_k | \hat{F}_1 | \varphi_n \rangle = 0. \end{aligned} \tag{2.79}$$

Substituting $\hat{F}_1$ and $\hat{F}_2$ according (2.73) to (2.79) and using the identity

$$\hat{J}_0|\varphi_m\rangle \equiv \hat{K}_0|\varphi_m\rangle \tag{2.80}$$

we see that relations (2.79) express that the right sides of the equations (2.75) – (2.77) are zero.

Thus, the following statement was proved. If the configurations are built on an orthonormal orbital set for which the first variation of an energy of the configuration $(-,m)$ vanishes, then the Hamiltonian matrix elements between this configuration and any of the configurations $(-,m')$ with $m' \neq m$, configuration (k,mm), and of the vector (2.55b) of the configuration (k,mn) with $n \neq m$ are equal to zero.

Generally the equation (2.72) has many solutions but the statement proved so far is valid for any particular solution irrespective of the procedure of its derivation. Thus, this statement remains valid for the SCF orbitals obtained by the Roothaan operator [19] or by the use of the one-electron Hamiltonian for one open shell [18].

2.6.4 Calculation of Certain One-particle Properties

The wave function for the state λ in the CI method is expanded over the basis vectors

$$|\lambda\rangle = \sum_q X_{q\lambda}|\psi_q\rangle \tag{2.81}$$

and the MO φ_i used to construct the primitive vectors are usually expressed as linear combination of orthonormal AO

$$\varphi_i = \sum_\mu C_{\mu i}\chi_\mu \ . \tag{2.82}$$

Observable physical properties are determined by the matrix elements mostly of the one-particle operator $\hat{Q}$

$$\langle\kappa|\hat{Q}|\lambda\rangle=\sum_{pq}X_{p\kappa}^{*}X_{q\lambda}\left\langle\psi_p\middle|\hat{Q}\middle|\psi_q\right\rangle . \tag{2.83}$$

Thus, one first needs to calculate the matrix elements of $\hat{Q}$ on the basis vectors.

If $\hat{Q}$ is a spin-free operator, analytical expressions for the matrix elements $\left\langle\psi_p\middle|\hat{Q}\middle|\psi_q\right\rangle$ for the configurations considered so far are obtained directly from the Hamiltonian matrix elements (2.57) – (2.68) by ignoring two-electron terms and changing F_{ij} to Q_{ij} and F_0 to an average value Q_0 of the operator $\hat{Q}$ in the vacuum state. In particular, for the calculation of the electronic density on atoms $P_{\mu\mu}^{\lambda\lambda}$ and bond orders $P_{\mu\nu}^{\lambda\lambda}$ in a state λ as well as transition electronic density on atoms $P_{\mu\mu}^{\kappa\lambda}$ corresponding to a transition from state κ to state λ one must take $C_{\mu i}^{*}C_{\mu j}$ and correspondingly $C_{\mu i}^{*}C_{\nu j}\equiv P_{ij}$ instead of Q_{ij} and Q_0 must be put equal to

$$2\sum_{i=1}^{n_F}C_{\mu i}^{*}C_{\nu i} .$$

In the zero differential overlap approximation a component of the transition moment are determined through corresponding atomic coordinates and transition density, for example:

$$\mu_{\chi}^{\kappa\lambda}=\sum_{\nu}\chi_{\nu}P_{\nu\nu}^{\kappa\lambda} . \tag{2.84}$$

When calculating the spin density $\rho_{\mu\nu}^{\lambda}$ in a state λ one meets with an operator $\hat{Q}$ which according to formula (2.12) depends on the spin variables being diagonal over them. We give final expressions for the matrix elements needed to calculate the spin density denoting

$$C_{\mu i}^{*}C_{\nu j}\equiv P_{ij} , \tag{2.85}$$

namely:

$$\left\langle {}^3\Psi'_1 \middle| 2\hat{S}_z \middle| {}^3\Psi_1 \right\rangle = \delta_{kk'} P_{m'm} + \delta_{mm'} P_{kk'}, \tag{2.86}$$

$$\left\langle {}^2\Psi'_1 \middle| 2\hat{S}_z \middle| {}^2\Psi_1 \right\rangle = P_{m'm} \tag{2.87}$$

$$\left\langle {}^2\Psi'_2 \middle| 2\hat{S}_z \middle| {}^2\Psi_2 \right\rangle = \delta_{mm'} P_{kk'} \tag{2.88}$$

$$\left\langle {}^2\Psi'_3 \middle| 2\hat{S}_z \middle| {}^2\Psi_3 \right\rangle = \frac{1}{6}[\delta_{kk'}(4\delta_{mm'}P_{n'n} - 2\delta_{nn'}P_{m'm} - \delta_{mn'}P_{m'n} - \delta_{nm'}P_{n'm}) - P_{kk'}(4\delta_{mm'}\delta_{nn'} - 5\delta_{nn'}\delta_{nm'})], \tag{2.89}$$

$$\left\langle {}^2\Psi'_4 \middle| 2\hat{S}_z \middle| {}^2\Psi_4 \right\rangle = \frac{1}{2}[\delta_{kk'}(2\delta_{nn'}P_{m'm} - \delta_{mn'}P_{m'n} - \delta_{nm'}P_{n'm}) - P_{kk'}(\delta_{mm'}\delta_{nn'} - \delta_{mn'}\delta_{nm'})], \tag{2.90}$$

$$\left\langle {}^2\Psi'_1 \middle| 2\hat{S}_z \middle| {}^2\Psi_2 \right\rangle = -\delta_{mm'} P_{km} \tag{2.91}$$

$$\left\langle {}^2\Psi'_1 \middle| 2\hat{S}_z \middle| {}^2\Psi_3 \right\rangle = -\frac{1}{\sqrt{6}}(2\delta_{mm'}P_{kn} + \delta_{nm'}P_{km}) \tag{2.92}$$

$$\left\langle {}^2\Psi'_1 \middle| 2\hat{S}_z \middle| {}^2\Psi_4 \right\rangle = -\frac{1}{\sqrt{2}}\delta_{nm'}P_{km} \tag{2.93}$$

$$\left\langle {}^2\Psi'_2 \middle| 2\hat{S}_z \middle| {}^2\Psi_3 \right\rangle = \frac{1}{\sqrt{6}}[\delta_{kk'}(\delta_{mm'}P_{m'n} - \delta_{nm'}P_{m'm}) + 3P_{kk'}\delta_{mm'}\delta_{nm'}], \tag{2.94}$$

$$\left\langle {}^2\Psi'_2 \middle| 2\hat{S}_z \middle| {}^2\Psi_4 \right\rangle = \frac{1}{\sqrt{2}}[\delta_{kk'}(-\delta_{mm'}P_{m'n} + \delta_{nm'}P_{m'm}) + P_{kk'}\delta_{mm'}\delta_{nm'}], \tag{2.95}$$

$$\left\langle {}^2\Psi'_3 \middle| 2\hat{S}_z \middle| {}^2\Psi_4 \right\rangle = \frac{1}{\sqrt{12}}[\delta_{kk'}(-\delta_{mn'}P_{m'n} + 3\delta_{nm'}P_{n'm}) + P_{kk'}(2\delta_{mm'}\delta_{nn'} + \delta_{mn'}\delta_{nm'})]. \tag{2.96}$$

The expression for ${}^3\rho^{\lambda}_{\mu\mu}$ derived in [9 , 20] by the determinantal method is obtained from (2.86) in a way described above.

2.7 Exact Solution for a Seven-electron System Using Full CI Method

General approach to calculation of the CI matrix elements (2.5 above) was also used to perform full CI computation which gives an exact solution for a model Hamiltonian used. The full CI calculation was done for π-electronic model of the benzyl radical containing seven π-electrons. The reason why just the benzyl radical was chosen to perform such a labor-consuming full CI computation is connected with a still not-resolved discrepancy between computed π-spin density distribution in benzyl radical and its ESR proton splitting well studied experimentally.

This being the situation when it seems desirable to examine the different characteristics of the ground state of benzyl radical as the approximation for the wave function is improved and approaches an exact eigenfunction of a given π-electronic Hamiltonian. We focus in this review only on technique how the restricted up to the full CI calculations were practically performed.

For a π-electronic shell of benzyl radical we used the traditional model based on the zero differential overlap approximation. Introducing creation $\hat{a}^{+}_{\mu\sigma}$ and annihilation $\hat{a}_{\mu\sigma}$ operators for an electron in atomic state μ with the spin σ and using the second quantization representation, the corresponding Hamiltonian is

$$\hat{H} = \sum_{\mu\nu\sigma} h^{core}_{\mu\nu} \hat{a}^{+}_{\mu\sigma} \hat{a}_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\sigma'} \gamma_{\mu\nu} \hat{a}^{+}_{\mu\sigma} \hat{a}^{+}_{\nu\sigma'} \hat{a}_{\nu\sigma'} \hat{a}_{\mu\sigma}, \tag{2.97}$$

where $h^{core}_{\mu\nu}$ are so called core integrals, and $\gamma_{\mu\nu}$ – electron repulsion integrals of π-electronic theory. Indexes μ and ν run over all AOs (2.in our case from 1 to 7), and spin indexes σ and σ' take values +1/2 or –1/2. Regular model of the benzyl radical with standard CC bond length was used. Full CI was also performed for “equillibrium” model of the benzyl radical.

Now it is proper for computations to pass from AOs to MOs. Formally, this can be done by the introduction of creation $\hat{a}^{+}_{\mu\sigma}$ and annihilation $\hat{a}_{\mu\sigma}$ operators for electrons in molecular states through the canonical transformation

$$\hat{a}_{\mu\sigma} = \sum_{i} C_{\mu i} \hat{A}_{i\sigma}, \quad \hat{a}^{+}_{\mu\sigma} = \sum_{i} C^{*}_{\mu i} \hat{A}^{+}_{i\sigma}, \tag{2.98}$$

where $C_{\mu i}$ are expansion coefficients of MO i over AOs. It is necessary that these expansion coefficients form a unitary matrix. Thus, the MOs will be orthonormalized and the commutation properties of the operators $\hat{A}^{+}_{i\sigma}$ and $\hat{A}_{i\sigma}$ will have the standard form. Substituting (2.98) into (2.97) one obtains

$$\hat{H} = \sum_{ij\sigma} h_{ij} \hat{A}^{+}_{i\sigma} \hat{A}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} (ij\,|\,kl) \hat{A}^{+}_{i\sigma} \hat{A}^{+}_{j\sigma'} \hat{A}_{l\sigma'} \hat{A}_{k\sigma}\,, \tag{2.99}$$

where

$$h_{ij} = \sum_{\mu\nu} C^{*}_{\mu i} C_{\nu j} h^{core}_{\mu\nu}\,, \tag{2.100}$$

$$(ij\,|\,kl) = \sum_{\mu\nu} C^{*}_{\mu i} C_{\mu k} C^{*}_{\nu j} C_{\nu l} \gamma_{\mu\nu}\,. \tag{2.101}$$

In our computations the Hamiltonian (2.99) was taken as initial one. For the MOs entering (2.100) and (2.101) we have chosen those which minimize the energy of the ground configuration of benzyl. The corresponding orbital coefficients were computed by the SCF method for an open shell configuration [9]. Choice of these orbitals seems to be most natural providing conservation of the alternant properties for the full as well as for certain truncated configurational sets. These orbitals possess proper symmetry and some of the CI matrix elements are zero [12] due to relations analogous to Brilloiun’s theorem. It should be noted that the results obtained with full CI are invariant to the choice of the basis orbitals [5].

2.7.1 Configurations and Energy Results

In the framework of the CI method the wave function is improved simply by extension of the configurational set. With a full set of configurations, the number of which is finite in our case, one obtains an exact eigenfunction for a given model Hamiltonian. The theory of the CI method is well known [5]. The wave function is expanded in Slater determinants. The expansion coefficients are determined by diagonalization of the CI matrix. Its order can be lowered essentially if instead of single Slater determinants their orthonormal linear combinations of proper symmetry and multiplicity are used. We utilized this general scheme using the second quantization formalism described above successively, which is equivalent to the traditional determinantal approach (see *e.g.* Appendix below). The ground state configuration of benzyl has symmetry ${}^2B_2$. In the π-electron approximation there are 212 excited configurations of the same symmetry. The distribution of these with the multiplicity of the excitation and with the number of unpaired electrons is given in Table 2.1.

Table 2.1

Number of excited configurations for the benzyl radical
depending on their type with corresponding number of the basis vectors
(in parenthesis).

Number of unpaired electrons	Multiplicity of excitation					
	1	2	3	4	5	6
1	4(2.4)	21(2.21)	24(2.24)	33(2.33)	12(2.12)	5(2.5)
3	5(2.10)	14(2.28)	36(2.72)	22(2.44)	13(2.26)	–
5	–	5(2.25)	8(2.40)	9(2.45)	–	–
7	–	–	1(2.14)	–	–	–
Σ	9(2.14)	40(2.74)	69(2.150)	64(2.122)	25(2.38)	5(2.5)

For each configuration one can form one or more orthonormal doublet basis vectors corresponding to a positive projection of the spin. Construction of such single vector for the configuration $(i)^2(j)^2(k)^2(l)^1$ is simple. This vector corresponds to a single Slater determinant and is written as

$$A^+_{i\alpha}A^+_{i\beta}A^+_{j\alpha}A^+_{j\beta}A^+_{k\alpha}A^+_{k\beta}A^+_{l\alpha}|0\rangle, \qquad (2.102)$$

where $|0\rangle$ is the vacuum state, and indices α and β denote values +1/2 and –1/2 of the spin variable σ.

The configuration $(i)^2(j)^2(k)^1(l)^1(m)^1$ with three unpaired electrons gives rise to three vectors of type (2.102) with $M_S = +1/2$:

$$A^{+}_{i\alpha}A^{+}_{i\beta}A^{+}_{j\alpha}A^{+}_{j\beta}\times\begin{cases} A^{+}_{k\alpha}A^{+}_{l\alpha}A^{+}_{m\beta}\left|0\right\rangle \\ A^{+}_{k\alpha}A^{+}_{l\beta}A^{+}_{m\alpha}\left|0\right\rangle \\ A^{+}_{k\beta}A^{+}_{l\alpha}A^{+}_{m\alpha}\left|0\right\rangle \end{cases}. \tag{2.103}$$

A linear combination of these configurations is written symbolically as

$$C_1\alpha\alpha\beta + C_2\alpha\beta\alpha + C_3\beta\alpha\alpha\ . \tag{2.104}$$

Two sets of coefficients $(1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$ and $(1/\sqrt{2}, -1/\sqrt{2}, 0)$ give the two orthonormal doublet basis vectors.

For configurations with five and seven unpaired electrons the number of different spin-configurations with $M_S = +1/2$ is equal to 10 and 35, and the number of possible mutually orthogonal basis vectors is equal to 5 and 14. The corresponding sets of coefficients in the linear combination of type (2.104) obtained by the VB method with subsequent orthogonalization are collected in Table 2.2. For convenience of listing these vectors are not normalized.

Table 2.2

Expansion coefficients of the basis vectors
with five unpaired electrons over spin-configurations.

Spin-configuration	Basis vectors				
αααββ	0	0	–1	–1	1
ααβαβ	0	0	1	1	1
αβααβ	2	0	0	0	–1
βαααβ	–2	0	0	0	–1
ααββα	0	0	–1	1	–1
αβαβα	–1	1	1	0	0
βααβα	1	–1	1	0	0
αββαα	–1	–1	0	–1	0

βαβαα	1	1	0	–1	0
ββααα	0	0	–1	1	1

Expansion coefficients of all 35 basis vectors with seven unpaired electrons over spin-configurations can be found in [21].

The number of possible doublet basis vectors corresponding to different types of configurations is indicated in parenthesis in Table 1.

The total number of basis vectors related to singly excited configurations of symmetry $^2B_2$ is equal to 14, doubly – to 74, triply – to 150, quadruply – to 122, quintuply – to 38, and sextuply – to 5.

Computations were performed with seven sets of basis vectors – G, I, II, III, IV, V, and F. Set G represents only the ground state configuration of benzyl. Each of the other sets was extended compared with previous one at the expense of the basis vectors corresponding to configurations of the next higher order of excitation.

Thus the size of the configurational sets used was equal to 1, 15, 89, 239, 361, and 404 correspondingly. Set F with 404 configurations corresponds to the wave function with full CI.

In order to perform CI computations one usually finds analytical expressions for matrix elements of the Hamiltonian over the basis vectors of different types. In our case this traditional way is not acceptable for most of the expressions to be programmed are cumbersome and the number of them is too large.

The derivation of the analytical expressions for the Hamiltonian matrix elements were rejected and entrusted this job to a computer at an early stage (standard procedure).

To do this it was necessary to program simple rules for calculation of the matrix elements in the second quantization representation which follow from Wick’s theorems and are equally good for configurations of arbitrary complexity. Necessary rules are given in p.5 above.

Occupation numbers of one-particle states for electrons are equal to 0 or 1. Therefore the computer code is ideally suitable to record vectors of type (2.102). The first eigenvalues and corresponding eigenvectors of the CI matrix were computed by an algorithm proposed by Nesbet.

The energy of the ground state of the benzyl radical computed with different configurational sets is given in Table 2.3.

Table 2.3

Change in energy *E* of the ground state of the benzyl radical and of the overlap integrals *S* between its exact and approximate wave functions as the configurational set is extending.

Configurational set	*E, eV*	*S*
G	0.929722	0.945313
I	0.760009	0.966577
II	0.058437	0.997981
III	0.021089	0.999471
IV	0.000394	0.999994
V	0.000082	0.999999
F	0*	1

* Energy of the benzyl radical computed with full CI was taken as zero and for parametrical Hamiltonian (2.97) was equal to –211.756817 *eV*.

The difference between the energy corresponding to full CI and the energy obtained in the single-configuration approximation will be called the correlation energy for a given model Hamiltonian.

It is seen from Table 2.3 that the correlation energy in our case is equal to –0.929722 *eV*. With the singly excited configurations only 18% of this energy is taken into account.

Extension of the orbitals basis to include doubly excited configurations leads to an account of almost all the correlation energy, namely 94%, though higher order corrections should be taken into account too.

We do not give many other demonstrative results which came out of these computations [21].

Our purpose was just to illustrate the second quantization technique described above to perform large scale CI calculations. Especially it is very effective in a case of the multiatomic molecular systems. More detailed information including computer program in ALGOL may be found in [23].

2.8 Appendix. Determinantal Method to Derive the Electron Density – Bond Order Matrix and the Spin Density with an Account of All Singly and Doubly Excited Configurations for Molecular States

The inclusion of more than singly excited configurations leads to a closer description of reactivity, geometry, and other properties of molecules in the ground and excited states. The knowledge of the distribution of the electron density $P_{\mu\mu}$, the spin density $\rho_{\mu\mu}$, and the bond orders $P_{\mu\nu}$ computed with an account of doubly excited configurations is important.

It is not difficult to find in quantum chemistry literature computations when wrong or better to say non-complete formulae for electron distributions mentioned above are used.

For example, formula for ${}^1P_{\mu\nu}$ used in [24] is valid only for the case of mixing of some particular doubly excited configurations, namely those of the types ${}^1\Phi_{\substack{i\to k\\ i\to k}}$ and ${}^1\Phi_{\substack{i\to k\\ j\to l}}$, and of the ground state configuration ${}^1\Phi_0$. Here the occupied MO's of the ground state of a molecule are designated by *i* and *j*, and the unoccupied – by *k* and *l*. The single-configurational wave function of the ground state of a molecule with 2*n* electrons is

$${}^1\Phi_0 = (1\bar{1}...i\bar{i}...j\bar{j}...n\bar{n})$$

or for the brevity just

$${}^1\Phi_0 = |i\bar{i}...j\bar{j}|.$$

An identical wrong formula was erroneously used in [25 – 27] where singly and/or doubly excited configurations of arbitrary types have been included. The correct formulae for ${}^{1,3}P_{\mu\nu}$ and $\rho_{\mu\mu}$ with the inclusion of only singly excited configurations can be found in [9] where also is mentioned that the use of the widely-spread simple formula [24 – 27] for mixing of configurations of arbitrary types leads to an even qualitatively incorrect electron density distribution, especially for the states of different multiplicity.

This appendix summarizes the derivation of the general expressions for ${}^{1,3}P_{\mu\nu}$ of the ground and excited singlet and triplet molecular states and for $\rho_{\mu\mu}$ of the triplet states by the determinantal method in the frame of the CI method including all singly and all doubly excited configurations [20].

2.8.1 The Wave Functions

The multi-configurational wave functions for the singlet and triplet states are

$$
\begin{aligned}
{}^1\Psi = {}^1X_0\,{}^1\Phi_0 &+ \sum {}^1X_{i\to k}\,{}^1\Phi_{i\to k} + \sum {}^1X_{\substack{i\to k\\ i\to k}}\,{}^1\Phi_{\substack{i\to k\\ i\to k}} + \sum {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1\Phi_{\substack{i\to k\\ j\to k}} + \\
&+ \sum {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1\Phi_{\substack{i\to k\\ i\to l}} + \sum {}^1X'_{\substack{i\to k\\ j\to l}}\,{}^1\Phi'_{\substack{i\to k\\ j\to l}} + \sum {}^1X''_{\substack{i\to k\\ j\to l}}\,{}^1\Phi''_{\substack{i\to k\\ j\to l}},
\end{aligned}
$$

$$
\begin{aligned}
{}^3\Psi = \sum {}^3X_{i\to k}\,{}^3\Phi_{i\to k} &+ \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3\Phi_{\substack{i\to k\\ j\to k}} + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3\Phi_{\substack{i\to k\\ i\to l}} + \\
&+ \sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3\Phi'_{\substack{i\to k\\ j\to l}} + \sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3\Phi''_{\substack{i\to k\\ j\to l}} + \sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3\Phi'''_{\substack{i\to k\\ j\to l}},
\end{aligned}
$$

where here and in the following equations the summation indexes over MO’s are omitted supposing that they run independently over all possible values, and

$$
{}^1\Phi_{i\to k} = \frac{1}{\sqrt{2}}(|i\bar{k}\,j\bar{j}\,| - |\,\bar{i}\,k\,j\bar{j}\,|), \quad {}^1\Phi_{\substack{i\to k\\ i\to k}} = |k\bar{k}\,j\bar{j}\,|, \quad {}^1\Phi_{\substack{i\to k\\ j\to k}} = \frac{1}{\sqrt{2}}(|i\bar{k}\,\bar{j}k\,| + |\,\bar{i}\,k\,j\bar{k}\,|),
$$

$$
{}^1\Phi_{\substack{i\to k\\ i\to l}} = \frac{1}{\sqrt{2}}(|k\bar{l}\,j\bar{j}\,| + |l\bar{k}\,j\bar{j}\,|), \quad {}^1\Phi'_{\substack{i\to k\\ j\to l}} = \frac{1}{2}(|i\bar{k}\,\bar{j}l\,| + |\,\bar{i}\,k\,j\bar{l}\,| - |ik\bar{j}\bar{l}\,| - |\,\bar{i}\,\bar{k}\,jl\,|),
$$

$$
{}^1\Phi''_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{12}}(|i\bar{k}\,\bar{j}l\,| + |\,\bar{i}\,k\,j\bar{l}\,| + |ik\bar{j}\bar{l}\,| + |\,\bar{i}\,\bar{k}\,jl\,| - 2\,|i\bar{k}\,j\bar{l}\,| - 2\,|\,\bar{i}\,k\,\bar{j}\,l\,|),
$$

$$
{}^3\Phi_{i\to k} = |ik\,j\bar{j}\,|, \quad {}^3\Phi_{\substack{i\to k\\ j\to k}} = |i\bar{k}\,jk\,|, \quad {}^3\Phi_{\substack{i\to k\\ i\to l}} = |kl\,j\bar{j}\,|, \quad {}^3\Phi'_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{2}}(|\,\bar{i}\,k\,jl\,| - |ik\,j\bar{l}\,|),
$$

$$
{}^3\Phi''_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{6}}(|\,\bar{i}\,k\,jl\,| + |ik\,j\bar{l}\,| - 2\,|ik\bar{j}\,l\,|), {}^3\Phi'''_{\substack{i\to k\\ j\to l}} = \frac{1}{\sqrt{12}}(|\,\bar{i}\,k\,jl\,| + |ik\,j\bar{l}\,| + |ik\bar{j}\,l\,| - 3\,|i\bar{k}\,jl\,|).
$$

2.8.2 The Expectation Value of a One-electron Operator

Let the one-electron operator be given

$$\hat{Q} = \sum_t \hat{Q}(t) .$$

There should be found its average values

$$^1\langle \hat{Q} \rangle = \langle {}^1\Psi | \hat{Q} | {}^1\Psi \rangle \text{ and } {}^3\langle \hat{Q} \rangle = \langle {}^3\Psi | \hat{Q} | {}^3\Psi \rangle .$$

In order to calculate the matrix elements of $\hat{Q}$ on the determinantal functions contained in ${}^1\Psi$ and ${}^3\Psi$ one may use the known expansion [5]

$$\langle U | \hat{Q} | V \rangle = \sum_{rs} \langle u_r | \hat{Q} | v_s \rangle D(r \mid s),$$

where

$$U = (u_1 u_2 u_3 ... u_N),$$

$$V = (v_1 v_2 v_3 ... v_N),$$

and $D(r \mid s)$ is a minor of the determinant

$$D = \langle U \mid V \rangle ,$$

received by crossing in D the column r and the row s .

Tedious calculations lead to the following expressions for ${}^1\langle \hat{Q} \rangle$ through the matrix elements of $\hat{Q}$ in the MO representation and for ${}^3\langle \hat{Q} \rangle$ in the spin-MO representations:

$$
\begin{aligned}
{}^1\left\langle \hat{Q} \right\rangle = {} & 2\sum_{i=1}^{n} Q_{ii} + \sum {}^1X_{i\to k}\,{}^1X_{i'\to k'}(Q_{kk'}\delta_{ii'} - Q_{ii'}\delta_{kk'}) + 2\sum {}^1X^{2}_{\substack{i\to k\\ i\to k}}(Q_{kk} - Q_{ii}) + \\
& + \sum {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1X_{\substack{i'\to k\\ j'\to k}}(2Q_{kk}\delta_{ii'}\delta_{jj'} - Q_{ii'}\delta_{jj'} - Q_{jj'}\delta_{ii'}) + \\
& + \sum {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1X_{\substack{i\to k'\\ i\to l'}}(-2Q_{ii}\delta_{kk'}\delta_{ll'} + Q_{ll'}\delta_{kk'} + Q_{kk'}\delta_{ll'}) + \\
& + \sum \left({}^1X'_{\substack{i\to k\\ j\to l}}\,{}^1X'_{\substack{i'\to k'\\ j'\to l'}} + {}^1X''_{\substack{i\to k\\ j\to l}}\,{}^1X''_{\substack{i'\to k'\\ j'\to l'}} \right)(Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + Q_{ll'}\delta_{ii'}\delta_{jj'}\delta_{kk'} - Q_{ii'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - Q_{jj'}\delta_{ii'}\delta_{kk'}\delta_{ll'}) + \\
& + 2\sqrt{2}\sum {}^1X_{i\to k}\left({}^1X_0 + {}^1X_{\substack{i\to k\\ i\to k}} \right)Q_{ik} - 2\sum {}^1X_{i\to k}\,{}^1X_{\substack{i\to k\\ j\to k}}Q_{jk} + 2\sum {}^1X_{i\to k}\,{}^1X_{\substack{i\to k\\ i\to l}}Q_{il} - \\
& - \sqrt{2}\sum {}^1X_{i\to k}\left({}^1X'_{\substack{i\to k\\ j\to l}} + \sqrt{3}\,{}^1X''_{\substack{i\to k\\ j\to l}} \right)Q_{jl} + 2\sqrt{2}\sum\left({}^1X_{\substack{i\to k\\ i\to k}}\,{}^1X_{\substack{i\to k\\ j\to k}} + {}^1X_{\substack{i\to k\\ i\to l}}\,{}^1X'_{\substack{i\to k\\ j\to l}} \right)Q_{ij} + \\
& + 2\sqrt{2}\sum\left({}^1X_{\substack{i\to k\\ i\to k}}\,{}^1X_{\substack{i\to k\\ i\to l}} + {}^1X_{\substack{i\to k\\ j\to k}}\,{}^1X'_{\substack{i\to k\\ j\to l}} \right)Q_{kl},
\end{aligned}
$$

$$
\begin{aligned}
{}^3\left\langle \hat{Q} \right\rangle = {} & \sum_{i=1}^{n}(Q_{ii} + Q_{\bar{i}\bar{i}}) + \sum {}^3X_{i\to k}\,{}^3X_{i'\to k'}(Q_{kk'}\delta_{ii'} - Q_{ii'}\delta_{kk'}) + \\
& + \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X_{\substack{i'\to k\\ j'\to k}}[(Q_{kk} + Q_{\bar{k}\bar{k}})\delta_{ii'}\delta_{jj'} - Q_{\bar{i}\bar{i}'}\delta_{jj'} - Q_{\bar{j}\bar{j}'}\delta_{ii'}] + \\
& + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X_{\substack{i\to k'\\ i\to l'}}[-(Q_{ii} + Q_{\bar{i}\bar{i}})\delta_{kk'}\delta_{ll'} + Q_{kk'}\delta_{ll'} + Q_{ll'}\delta_{kk'}] + \\
& + \sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3X'_{\substack{i'\to k'\\ j'\to l'}}[Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} - Q_{\bar{j}\bar{j}'}\delta_{ii'}\delta_{kk'}\delta_{ll'} + \tfrac{1}{2}(Q_{ll'} + Q_{\bar{l}\bar{l}'})\delta_{ii'}\delta_{jj'}\delta_{kk'} - \\
& - \tfrac{1}{2}(Q_{ll'} + Q_{\bar{l}\bar{l}'})\delta_{ii'}\delta_{jj'}\delta_{kk'}] + \frac{1}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X''_{\substack{i'\to k'\\ j'\to l'}}[6Q_{kk'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + (5Q_{ll'} + Q_{\bar{l}\bar{l}'})\delta_{ii'}\delta_{jj'}\delta_{ll'} - \\
& - (4Q_{\bar{j}\bar{j}'} + 2Q_{\bar{j}\bar{j}'})\delta_{ii'}\delta_{kk'}\delta_{ll'} - (Q_{ii'} + 5Q_{\bar{i}\bar{i}'})\delta_{jj'}\delta_{kk'}\delta_{ll'}] + \frac{1}{12}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}[(3Q_{kk'} + \\
& + 9Q_{\bar{k}\bar{k}'})\delta_{ii'}\delta_{jj'}\delta_{ll'} + (11Q_{ll'} + Q_{\bar{l}\bar{l}'})\delta_{ii'}\delta_{jj'}\delta_{kk'} - (Q_{ii'} + 11Q_{\bar{i}\bar{i}'})\delta_{jj'}\delta_{kk'}\delta_{ll'} - \\
& - (11Q_{\bar{j}\bar{j}'} + Q_{jj'})\delta_{ii'}\delta_{kk'}\delta_{ll'}] - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ j\to k}}Q_{\bar{j}\bar{k}} - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ i\to l}}Q_{il} - \\
& - \sqrt{2}\sum {}^3X_{i\to k}\,{}^3X'_{\substack{i\to k\\ j\to l}}Q_{\bar{j}\bar{l}} + \sqrt{\frac{2}{3}}\sum {}^3X_{i\to k}\,{}^3X''_{\substack{i\to k\\ j\to l}}(2Q_{jl} + Q_{\bar{j}\bar{l}}) + \frac{1}{\sqrt{3}}\sum {}^3X_{i\to k}\,{}^3X'''_{\substack{i\to k\\ j\to l}}(Q_{\bar{j}\bar{l}} - Q_{jl}) + \\
& + \sqrt{2}\sum {}^3X'_{\substack{i\to k\\ j\to k}}\left({}^3X'_{\substack{i\to k\\ j\to l}} - \frac{1}{\sqrt{3}}\,{}^3X''_{\substack{i\to k\\ j\to l}} \right)Q_{\bar{k}\bar{l}} - \frac{1}{\sqrt{3}}\sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}(3Q_{kl} + Q_{\bar{k}\bar{l}}) + \\
& + \sqrt{2}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X'_{\substack{i\to k\\ j\to l}}Q_{\bar{i}\bar{j}} + \sqrt{\frac{2}{3}}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X''_{\substack{i\to k\\ j\to l}}(Q_{\bar{i}\bar{j}} + 2Q_{ij}) + \frac{1}{\sqrt{3}}\sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X'''_{\substack{i\to k\\ j\to l}}(Q_{\bar{i}\bar{j}} - Q_{ij}) + \\
& + \frac{1}{\sqrt{3}}\sum\left[{}^3X'_{\substack{i\to k\\ j\to l}}\left({}^3X''_{\substack{i'\to k\\ j\to l'}} + \frac{1}{\sqrt{2}}\,{}^3X'''_{\substack{i'\to k\\ j\to l'}} \right) \right][(Q_{ll'} - Q_{\bar{l}\bar{l}'})\delta_{ii'} + (Q_{\bar{i}\bar{i}'} - Q_{ii'})\delta_{ll'}] + \\
& + \frac{\sqrt{2}}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k\\ j'\to l'}}[(Q_{\bar{l}\bar{l}'} - Q_{ll'})\delta_{ii'}\delta_{jj'} + (Q_{\bar{i}\bar{i}'} - Q_{ii'})\delta_{jj'}\delta_{ll'} + 2(Q_{jj'} - Q_{\bar{j}\bar{j}'})\delta_{ii'}\delta_{ll'}]. \qquad (A1)
\end{aligned}
$$

2.8.3 The Electron Density – Bond Order Matrix and the Spin Density

Expanding the MOs in linear combination of AOs

$$\varphi_r = \sum_{\mu} C_{\mu r} \chi_{\mu} \qquad \text{(A2)}$$

one can introduce the matrix elements

$$Q_{\mu\nu} = \left\langle \chi_{\mu} \middle| \hat{Q} \middle| \chi_{\nu} \right\rangle$$

and obtains an expression for ${}^{1}\langle \hat{Q} \rangle$ in terms of the expansion coefficients $C_{\mu r}$.

Comparing it with the known expression

$$ {}^{1,3}\langle \hat{Q} \rangle = \sum_{\mu\nu} {}^{1,3}P_{\mu\nu} Q_{\mu\nu} \qquad (A3)$$

one finally obtains

$$\begin{aligned}
{}^{1}P_{\mu\nu} = {} & 2\sum_{i=1}^{n} C_{\mu i} C_{\nu i} + \sum {}^{1}X_{i\to k}\, {}^{1}X_{i'\to k'} (C_{\mu k} C_{\nu k'} \delta_{ii'} - C_{\mu i} C_{\nu i'} \delta_{kk'}) + 2\sum {}^{1}X^{2}_{\substack{i\to k \\ i\to k}} (C_{\mu k} C_{\nu k} - C_{\mu i} C_{\nu i}) + \\
& + \sum {}^{1}X_{\substack{i\to k \\ j\to k}}\, {}^{1}X_{\substack{i'\to k \\ j'\to k}} (2C_{\mu k} C_{\nu k} \delta_{ii'} \delta_{jj'} - C_{\mu i} C_{\nu i'} \delta_{jj'} - C_{\mu j} C_{\nu j'} \delta_{ii'}) + \\
& + \sum {}^{1}X_{\substack{i\to k \\ i\to l}}\, {}^{1}X_{\substack{i\to k' \\ i\to l'}} (-2C_{\mu i} C_{\nu i} \delta_{kk'} \delta_{ll'} + C_{\mu k} C_{\nu k'} \delta_{ll'} + C_{\mu l} C_{\nu l'} \delta_{kk'}) + \\
& + \sum \left({}^{1}X'_{\substack{i\to k \\ j\to l}}\, {}^{1}X'_{\substack{i'\to k' \\ j'\to l'}} + {}^{1}X''_{\substack{i\to k \\ j\to l}}\, {}^{1}X''_{\substack{i'\to k' \\ j'\to l'}} \right) (C_{\mu k} C_{\nu k'} \delta_{ii'} \delta_{jj'} \delta_{ll'} + C_{\mu l} C_{\nu l'} \delta_{ii'} \delta_{jj'} \delta_{kk'} - C_{\mu i} C_{\nu i'} \delta_{jj'} \delta_{kk'} \delta_{ll'} - \\
& - C_{\mu j} C_{\nu j'} \delta_{ii'} \delta_{kk'} \delta_{ll'}) + 2\sqrt{2} \sum {}^{1}X_{i\to k} \left({}^{1}X_{0} + {}^{1}X_{\substack{i\to k \\ i\to k}} \right) C_{\mu i} C_{\nu k} - 2\sum {}^{1}X_{i\to k}\, {}^{1}X_{\substack{i\to k \\ j\to k}} C_{\mu j} C_{\nu k} + \\
& + 2\sum {}^{1}X_{i\to k}\, {}^{1}X_{\substack{i\to k \\ i\to l}} C_{\mu i} C_{\nu l} - \sqrt{2} \sum {}^{1}X_{i\to k} \left({}^{1}X'_{\substack{i\to k \\ j\to l}} + \sqrt{3}\, {}^{1}X''_{\substack{i\to k \\ j\to l}} \right) C_{\mu j} C_{\nu l} + \\
& + 2\sqrt{2} \sum \left({}^{1}X_{\substack{i\to k \\ i\to k}}\, {}^{1}X_{\substack{i\to k \\ j\to k}} + {}^{1}X_{\substack{i\to k \\ i\to l}}\, {}^{1}X'_{\substack{i\to k \\ j\to l}} \right) C_{\mu i} C_{\nu j} + \\
& + 2\sqrt{2} \sum \left({}^{1}X_{\substack{i\to k \\ i\to k}}\, {}^{1}X_{\substack{i\to k \\ i\to l}} + {}^{1}X_{\substack{i\to k \\ j\to k}}\, {}^{1}X'_{\substack{i\to k \\ j\to l}} \right) C_{\mu k} C_{\nu l}. \qquad (A4)
\end{aligned}$$

In order to calculate $\rho_{\mu\mu}$ let put in $(A1)$

$$\hat{Q} = \sum_t \hat{S}_z(t)$$

Taking into account that

$$(\hat{S}_z)_{ij} = -(\hat{S}_z)_{\bar{i}\,\bar{j}}$$

and using the AO basis one obtains after some manipulations

$$\begin{aligned}
\left\langle \sum_t \hat{S}_z(t) \right\rangle = {} & \frac{1}{2}\sum {}^3X_{i\to k}\, {}^3X_{i'\to k'} \sum_\mu (C_{\mu k}C_{\mu k'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{kk'}) + \\
& + \frac{1}{2}\sum {}^3X_{\substack{i\to k\\ j\to k}}\, {}^3X_{\substack{i'\to k\\ j'\to k}} \sum_\mu (C_{\mu j}C_{\mu j'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{jj'}) + \frac{1}{2}\sum {}^3X_{\substack{i\to k\\ i\to l}}\, {}^3X_{\substack{i\to k'\\ i\to l'}} \sum_\mu (C_{\mu k}C_{\mu k'}\delta_{ll'} + C_{\mu l}C_{\mu l'}\delta_{kk'}) \\
& + \frac{1}{2}\sum {}^3X'_{\substack{i\to k\\ j\to l}}\, {}^3X'_{\substack{i\to k'\\ j'\to l}} \sum_\mu (C_{\mu k}C_{\mu k'}\delta_{jj'} + C_{\mu j}C_{\mu j'}\delta_{kk'}) + \frac{1}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\, {}^3X''_{\substack{i'\to k'\\ j'\to l'}} \sum_\mu (3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + \\
& + 2C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} + 2C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'}) + \\
& + \frac{1}{12}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}\, {}^3X'''_{\substack{i'\to k'\\ j'\to l'}} \sum_\mu (5C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} + 5C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'} + 5C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} - \\
& - 3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}) + \sum {}^3X_{i\to k}\, {}^3X_{\substack{i\to k\\ j\to k}} \sum_\mu C_{\mu j}C_{\mu k} - \sum {}^3X_{i\to k}\, {}^3X_{\substack{i\to k\\ i\to l}} \sum_\mu C_{\mu i}C_{\mu l} + \\
& + \frac{1}{2}\sum {}^3X_{i\to k}\left(\sqrt{2}\, {}^3X'_{\substack{i\to k\\ j\to l}} + \sqrt{\frac{2}{3}}\, {}^3X''_{\substack{i\to k\\ j\to l}} - \frac{2}{\sqrt{3}}\, {}^3X'''_{\substack{i\to k\\ j\to l}} \right) \sum_\mu C_{\mu j}C_{\mu l} + \frac{1}{2}\sum {}^3X_{\substack{i\to k\\ j\to k}} (-\sqrt{2}\, {}^3X'_{\substack{i\to k\\ j\to l}} + \\
& + \sqrt{\frac{2}{3}}\, {}^3X''_{\substack{i\to k\\ j\to l}} - \frac{2}{\sqrt{3}}\, {}^3X'''_{\substack{i\to k\\ j\to l}}) \sum_\mu C_{\mu k}C_{\mu l} + \frac{1}{2}\sum {}^3X_{\substack{i\to k\\ i\to l}} (-\sqrt{2}\, {}^3X'_{\substack{i\to k\\ j\to l}} + \sqrt{\frac{2}{3}}\, {}^3X''_{\substack{i\to k\\ j\to l}} - \frac{2}{\sqrt{3}}\, {}^3X'''_{\substack{i\to k\\ j\to l}}) \sum_\mu C_{\mu i}C_{\mu j} \\
& + \frac{1}{\sqrt{3}}\sum {}^3X'_{\substack{i\to k\\ j\to l}} \left({}^3X''_{\substack{i'\to k\\ j\to l'}} + \frac{1}{\sqrt{2}}\, {}^3X'''_{\substack{i'\to k\\ j\to l'}} \right) \sum_\mu (C_{\mu l}C_{\mu l'}\delta_{ii'} - C_{\mu i}C_{\mu i'}\delta_{ll'}) + \\
& + \frac{\sqrt{2}}{6}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\, {}^3X'''_{\substack{i'\to k\\ j'\to l'}} \sum_\mu (2C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{ll'} - C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{ll'} - C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}).
\end{aligned}$$

On the other hand $\left\langle \sum_t \hat{S}_z(t) \right\rangle = \frac{1}{2}\sum_\mu \rho_{\mu\mu}$, so that finally

$$
\begin{aligned}
\rho_{\mu\mu} = {} & \sum {}^3X_{i\to k}\,{}^3X_{i'\to k'}(C_{\mu k}C_{\mu k'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{kk'}) + \\
& + \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X_{\substack{i'\to k\\ j'\to k}}(C_{\mu j}C_{\mu j'}\delta_{ii'} + C_{\mu i}C_{\mu i'}\delta_{jj'}) + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X_{\substack{i\to k'\\ i\to l'}}(C_{\mu k}C_{\mu k'}\delta_{ll'} + C_{\mu l}C_{\mu l'}\delta_{kk'}) + \\
& + \sum {}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3X'_{\substack{i\to k'\\ j'\to l}}(C_{\mu k}C_{\mu k'}\delta_{jj'} + C_{\mu j}C_{\mu j'}\delta_{kk'}) + \frac{1}{3}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X''_{\substack{i'\to k'\\ j'\to l'}}(3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + \\
& + 2C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} + 2C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'}) + \\
& + \frac{1}{6}\sum {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}(5C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} + 5C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'} + 5C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} - \\
& - 3C_{\mu k}C_{\mu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'}) + 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ j\to k}}C_{\mu j}C_{\mu k} - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\mu l} + \\
+ & \sqrt{\frac{2}{3}}\sum {}^3X_{i\to k}\left(\sqrt{3}\,{}^3X'_{\substack{i\to k\\ j\to l}} + {}^3X''_{\substack{i\to k\\ j\to l}} - \sqrt{2}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\right)C_{\mu j}C_{\mu l} + \sqrt{\frac{2}{3}}\sum(-\sqrt{3}\,{}^3X'_{\substack{i\to k\\ j\to l}} + {}^3X''_{\substack{i\to k\\ j\to l}} - \sqrt{2}\,{}^3X'''_{\substack{i\to k\\ j\to l}})\times \\
& \times({}^3X_{\substack{i\to k\\ j\to k}}C_{\mu k}C_{\mu l} + {}^3X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\mu j}) + \sqrt{\frac{2}{3}}\sum {}^3X'_{\substack{i\to k\\ j\to l}}\left(\sqrt{2}\,{}^3X''_{\substack{i'\to k\\ j\to l'}} + {}^3X'''_{\substack{i'\to k\\ j\to l'}}\right)(C_{\mu l}C_{\mu l'}\delta_{ii'} - C_{\mu i}C_{\mu i'}\delta_{ll'}) \\
& + \frac{\sqrt{2}}{3}\sum {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k\\ j'\to l'}}(2C_{\mu j}C_{\mu j'}\delta_{ii'}\delta_{ll'} - C_{\mu i}C_{\mu i'}\delta_{jj'}\delta_{ll'} - C_{\mu l}C_{\mu l'}\delta_{ii'}\delta_{jj'}). \qquad (A5)
\end{aligned}
$$

The expression (A1) also permits to obtain the formula for ${}^3P_{\mu\nu}$. Let us carry out the summation in (A1) over the spin variables taking the normalization condition of ${}^3\Psi$ into account. Using the AO representation and comparing the expression derived so far with (A3) one finally obtains

$$
\begin{aligned}
{}^3P_{\mu\nu} = {} & 2\sum_{i=1}^{n} C_{\mu i}C_{\nu i} + \sum {}^3X_{i\to k}\,{}^3X_{i'\to k'}(C_{\mu k}C_{\nu k'}\delta_{ii'} - C_{\mu i}C_{\nu i'}\delta_{kk'}) + \\
& + \sum {}^3X_{\substack{i\to k\\ j\to k}}\,{}^3X_{\substack{i'\to k\\ j'\to k}}(2C_{\mu k}C_{\nu k}\delta_{ii'}\delta_{jj'} - C_{\mu i}C_{\nu i'}\delta_{jj'} - C_{\mu j}C_{\nu j'}\delta_{ii'}) + \\
& + \sum {}^3X_{\substack{i\to k\\ i\to l}}\,{}^3X_{\substack{i\to k'\\ i\to l'}}(-2C_{\mu i}C_{\nu i}\delta_{kk'}\delta_{ll'} + C_{\mu k}C_{\nu k'}\delta_{ll'} + C_{\mu l}C_{\nu l'}\delta_{kk'}) + \\
& + \sum\left({}^3X'_{\substack{i\to k\\ j\to l}}\,{}^3X'_{\substack{i'\to k'\\ j'\to l'}} + {}^3X''_{\substack{i\to k\\ j\to l}}\,{}^3X''_{\substack{i'\to k'\\ j'\to l'}} + {}^3X'''_{\substack{i\to k\\ j\to l}}\,{}^3X'''_{\substack{i'\to k'\\ j'\to l'}}\right)(C_{\mu k}C_{\nu k'}\delta_{ii'}\delta_{jj'}\delta_{ll'} + C_{\mu l}C_{\nu l'}\delta_{ii'}\delta_{jj'}\delta_{kk'} - \\
& - C_{\mu i}C_{\nu i'}\delta_{jj'}\delta_{kk'}\delta_{ll'} - C_{\mu j}C_{\nu j'}\delta_{ii'}\delta_{kk'}\delta_{ll'}) + 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ j\to k}}C_{\mu j}C_{\nu k} - \\
& - 2\sum {}^3X_{i\to k}\,{}^3X_{\substack{i\to k\\ i\to l}}C_{\mu i}C_{\nu l} - \sqrt{2}\sum {}^3X_{i\to k}\left({}^3X'_{\substack{i\to k\\ j\to l}} - \sqrt{3}\,{}^3X''_{\substack{i\to k\\ j\to l}}\right)C_{\mu j}C_{\nu l} + \\
& + \sqrt{\frac{2}{3}}\sum {}^3X_{\substack{i\to k\\ j\to k}}\left(\sqrt{3}\,{}^3X'_{\substack{i\to k\\ j\to l}} - {}^3X''_{\substack{i\to k\\ j\to l}} - 2\sqrt{2}\,{}^3X'''_{\substack{i\to k\\ j\to l}}\right)C_{\mu k}C_{\nu l} + \\
& + \sqrt{2}\sum {}^3X'_{\substack{i\to k\\ j\to l}}\left({}^3X'_{\substack{i\to k\\ j\to l}} + \sqrt{3}\,{}^3X''_{\substack{i\to k\\ j\to l}}\right)C_{\mu i}C_{\nu j}. \qquad (A6)
\end{aligned}
$$

The expressions (A4) – (A6) immediately lead to the formulae [9]

$$^{1,3}P_{\mu\nu} = 2\sum_{i=1}^{n} C_{\mu i}C_{\nu i} + \sum {}^{1,3}X_{i\to k}\,{}^{1,3}X_{i'\to k'}(C_{\mu k}C_{\nu k'}\delta_{ii'} - C_{\mu i}C_{\nu i'}\delta_{kk'})\,, \qquad (A7)$$

and

$$\rho_{\mu\mu} = \sum {}^{3}X_{i\to k}\,{}^{3}X_{i'\to k'}(C_{\mu k}C_{\nu k'}\delta_{ii'} - C_{\mu i}C_{\nu i'}\delta_{kk'})\,, \qquad (A8)$$

which are valid for the case of including only singly excited configurations.

The formula for $^{1}P_{\mu\nu}$ erroneously used in [24 – 26] may be obtained from (*A*7) if the summation in the latter is restricted by the condition $i = i'$ and $k = k'$.

The validity of the expression for $^{1}P_{\mu\nu}$ used in [24] follows from (*A*4) when accounting only for some particular configurations, namely those of the type $^{1}\Phi_{0}$, $^{1}\Phi_{\substack{i\to k\\ i\to k}}$, and $^{1}\Phi_{\substack{i\to k\\ j\to l}}$ which have been included by the authors.

2.9 Conclusions

The second quantization method has been intensively developed and is widely used for treating many-particle problems. Kouba and Ohrn [28], for example, have considered and solved some of the problems which we discuss in a different way, namely a translation was made of spin projection methods into the language of second quantization. This leads to a new formula for the Sanibel coefficients and expressions convenient to use for automatic calculation of spin projections.

We discussed in this review only one aspect of the second quantization method, namely the construction of the multi-configurational wave functions. Our approach is alternative to the usual determinantal method but offers some advantages. The use of the second quantization representation allows the hole which is introduced naturally and which is a mathematical description of the interpretation of the excited configurations in terms of the particles and holes against the vacuum state.

The importance of this interpretation is obvious, particularly if the vacuum state is chosen as the Hartree – Fock state. Then the terms with the *N*-products in the Hamiltinian (2.34) will describe the correlation of the electrons in an explicit form.

Introduction of the hole formalism allows the expressions for the CI matrix elements in a form when the integrals of interaction with the vacuum particles are already summed up, and the vacuum state plays the role of an external field. The use of these expressions reduces the number of summations to a minimum which is essential when the number of particles is large. Despite the relative complexity of the second quantization method it reduces the procedure for the calculations of the matrix elements to a simple logical scheme which can be easily programmed.

The corresponding algorithm is universal for all varieties of the matrix elements met in actual computations and reduces to a few simple cases.

Such an algorithm which is based on this logical scheme for CI method was developed.

The corresponding program CI-2 is given in details in [23]. We have used this program repeatedly, in particularly for computing electronic states of benzyl radical [29], and glycine and tyrosine molecules and their neutral and charged radicals [30]. The same logical scheme, but without use of the hole formalism, was incorporated in program CI-3 to perform a complete CI for the benzyl radical [21].

Chapter 3.

RELATIVISTIC MANY-BODY PERTURBATION THEORY APPROACH TO CALCULATING ENERGY LEVELS, HYPERFINE STRUCTURE CONSTANTS FOR HEAVY ATOMS AND IONS

3.1 Introduction

In this chapter the relativistic calculation of the spectra hyperfine structure parameters for heavy atoms and multicharged ions with account of relativistic, correlation, nuclear, QED effects is carried out (the Superatom package) [31-38]. Our calculation scheme is based on gauge-invariant QED perturbation theory with using the optimized one-quasiparticle representation at first in the theory of the hyperfine structure for relativistic systems [2]. It is carried out calculating the energies and constants of the hyperfine structure, deriviatives of the one-electron characteristics on nuclear radius, nuclear electric quadrupole, magnetic dipole moments *Q* for atom of hydrogen ^{1}H (test calculation), superheavy H-like ion with nuclear charge Z=170, Li-like multicharged ions with Z=20-100, neutral atoms of ^{235}U, ^{201}Hg and ^{227}Ra are defined.

In last years a studying the spectra of heavy and superheavy elements atoms and ions is of a great interest for further development as atomic and nuclear theories (c.f.[31-38]).

Theoretical methods used to calculate the spectroscopic characteristics of heavy and superheavy ions may be divided into three main groups: a) the multi-configuration Hartree-Fock method, in which relativistic effects are taken into account in the Pauli approximation, gives a rather rough approximation, which makes it possible to get only a qualitative idea on the spectra of heavy ions. b) The multi-configuration Dirac-Fock (MCDF) approximation (the Desclaux program, Dirac package) [3] is, within the last few years, the most reliable version of calculation for multielectron systems with a large nuclear charge; in these calculations one- and two-particle relativistic effects are taken into account practically precisely.

The calculation program of Desclaux is compiled with proper account of the finiteness of the nucleus size; however, a detailed description of the method of their investigation of the role of the nucleus size is lacking. In the region of small Z (Z is a charge of the nucleus) the calculation error in the MCDF approximation is connected mainly with incomplete inclusion of the correlation and exchange effects which are only weakly dependent on Z; c)

In the study of lower states for ions with $Z \leq 40$ an expansion into double series of the PT on the parameters 1/Z, αZ (α is the fine structure constant) turned out to be quite useful. It permits evaluation of relative contributions of the different expansion terms: non-relativistic, relativistic, QED contributions as the functions of Z.

Nevertheless, the serious problems in calculation of the heavy elements spectra are connected with developing new, high exact methods of account for the QED effects, in particular, the Lamb shift (LS), self-energy (SE) part of the Lamb shift, vacuum polarization (VP) contribution, correction on the nuclear finite size for superheavy elements and its account for different spectral properties of these systems, including calculating the energies and constants of the hyperfine structure, deriviatives of the one-electron characteristics on nuclear radius, nuclear electric quadrupole, magnetic dipole moments etc (c.f.[2,31-38]).

In present paper a new, highly exact, ab initio approach to relativistic calculation of the spectra for multi-electron superheavy ions with an account of relativistic, correlation, nuclear, radiative effects is presented. The method is based on the quantum electrodynamical (QED) perturbation theory (PT). Relativistic calculation of the spectra hyperfine structure parameters for heavy atoms and multicharged ions with account of relativistic, correlation, nuclear, QED effects is carried out (the Superatom and Dirac packages (DP) are used; the DP using in a progress).

Our calculation scheme is based on gauge-invariant QED perturbation theory and and generelized relativistic dynamical effective field nuclear model with using the optimized one-quasiparticle representation at first in the theory of the hyperfine structure for relativistic systems [2].

The wave function zeroth basis is found from the Dirac equation with potential, which includes the core ab initio potential, the electric and polarization potentials of a nucleus (the gaussian form of charge distribution in the nucleus is considered) [31-38]. The correlation corrections of the high orders are taken into account within the Green functions method (with the use of the Feynman diagram's technique).

There have taken into account all correlation corrections of the second order and dominated classes of the higher orders diagrams (electrons screening, particle-hole interaction, mass operator iterations) [11-18]. The magnetic inter-electron interaction is accounted in the lowest (on α^2 parameter), the LS polarization part - in the Uehling-Serber approximation, self-energy part of the LS is accounted effectively within the Ivanov-Ivanova non-perturbative procedure [11].

Generelized relativistic dynamical effective field nuclear model is presented in [38] (see also refs.[2]). The energies and constants of the hyperfine structure, deriviatives of the one-electron characteristics on nuclear radius, nuclear electric quadrupole, magnetic dipole moments Q for atom of hydrogen ^{1}H (test calculation), superheavy H-like ion with nuclear charge Z=170, Li-like multicharged ions with Z=20-100, neutral atoms of ^{235}U, ^{201}Hg and ^{227}Ra are calculated.

3.2 Relativistic perturbation theory method for calculation of heavy and superheavy ions

Let us describe the key moments of our approach to relativistic calculation of the spectra for multi-electron superheavy ions with an account of relativistic, correlation, nuclear, radiative effects (more details can be found in ref.[31-38]).

3.2.1 Definition of the basis of relativistic orbitals

One-particle wave functions are found from solution of the relativistic Dirac equation, which can be written in the central field in a two-component form:

$$\frac{\partial F}{\partial r} + (1+\chi)\frac{F}{r} - (\varepsilon + m - v)G = 0$$

$$\frac{\partial G}{\partial r} + (1-\chi)\frac{G}{r} + (\varepsilon - m - v)F = 0 \qquad (3.1)$$

Here we put the fine structure constant α =1 . The moment number

$$\chi = \begin{cases} -(1+1), & j > 1 \\ 1, & j < 1 \end{cases} \qquad (3.2)$$

At large χ the radial functions F and G vary rapidly at the origin of co-ordinates:

$$\begin{aligned} &F(r), G(r) \approx r^{\gamma - 1} \\ &\gamma = \sqrt{\chi^2 - \alpha^2 z^2} \end{aligned} \qquad (3.3)$$

This involves difficulties in numerical integration of the equations in the region $r \to 0$. To prevent the integration step becoming too small it is convenient to turn to new functions isolating the main power dependence: $f = Fr^{1-|\chi|}$, $g = Gr^{1-|\chi|}$. The Dirac equation for F and G components are transformed as:

$$\begin{aligned} &f' = -(\chi + |\chi|) f/r - \alpha Z V g - (\alpha Z E_{n\chi} + 2/\alpha Z) g \\ &g' = (\chi - |\chi|) g/r - \alpha Z V f + \alpha Z E_{n\chi} f \end{aligned} \qquad (3.4)$$

Here the Coulomb units (C.u.) are used; 1 C.u. of length = 1 a.u.Z; 1 C.u. of energy = 1 a.u. Z^2. In Coulomb units the atomic characteristics vary weakly with Z. $E_{n\chi}$ is one-electron energy without the rest energy, the system of equations (4) has two fundamental, solutions. We are interested in the solution regular at $r \to 0$.

The boundary values of the correct solution are found by the first term s of the expansion into the Taylor series:

$$g = \left(V(0) - E_{n\chi}\right) r\alpha Z/(2\chi+1); \quad f = 1 \text{ at } \chi < 0$$

$$f = \left(V(0) - E_{n\chi} - 2/\alpha^2 Z^2\right)\alpha Z; \quad g = 1 \text{ at } \chi > 0$$

(3.5)

The condition $f, g \to 0$ at $r \to \infty$ determines the quantified energies of the state $E_{n\chi}$. At correctly determined energy $E_{n\chi}$ of the asymptotic f and g at $r \to \infty$ are:

$$f, g \sim \exp\left(-r/n^*\right) \tag{3.6}$$

where $n^* = \sqrt{1/2|E_{n\chi}|}$ is the effective main quantum number.

The equations (4) were solved by the Runge-Kutter method. The initial integration point $r_0 = R/10^6$, where R is the nucleus radius, the end of the integration interval is determined as

$$r_k \approx 30n^*.$$

3.3 Nuclear potential

Earlier we calculated some characteristics of hydrogen-like ions with the nucleus in the form of a uniformly charged sphere; analogous calculations by means of an improved model were also made; Here the smooth Gaussian function of the charge distribution in the nucleus is used. Using the smooth distribution function (instead of the discontinuous one) simplifies the calculation procedure and permits flexible simulation of the real distribution of the charge in the nucleus.

As in ref. [32] we set the charge distribution in the nucleus $\rho(r)$ by the Gaussian function. With regard to normalization we have:

$$\rho(r|R) = \left(4\gamma^{3/2}/\sqrt{\pi}\right)\exp\left(-\gamma r^2\right) \tag{3.7}$$

$$\int_0^\infty drr^2\rho(r|R) = 1; \quad \int_0^\infty drr^3\rho(r|R) = R$$

were $\gamma = 4/\pi R^2$, R is the effective nucleus radius.

The following simple dependence of *R* on *Z* assumed:

$$R = 1.60\times 10^{-13} z^{1/3}\ (cm) \tag{3.8}$$

Such definition of R is rather conventional.

We assume it as some zeroth approximation. Further the derivatives of various characteristics on R are calculated. They describe the interaction of the nucleus with outer electron; this permits recalculation of results, when R varies within reasonable limits.

The Coulomb potential for the spherically symmetric charge density $\rho(r|R)$ is:

$$V_{nucl}(r|R) = -((1/r)\int_0^r dr' r'^2\rho\left(r'\middle|R\right) + \int_r^\infty dr' r'\rho\left(r'\middle|R\right) \tag{3.9}$$

It is determined by the following system of differential equations:

$$V' nucl(r,R) = \left(1/r^2\right)\int_0^r dr' r'^2\rho\left(r',R\right) \equiv \left(1/r^2\right)y(r,R) \tag{3.10}$$

$$y'(r,R)=r^2\rho(r,R) \tag{3.11}$$

$$\rho'(r,R)=-8\gamma^{5/2}\ r/\sqrt{\pi}\ \exp\left(-\gamma r^2\right)=-2\gamma r\rho(r,R)=-\frac{8r}{\pi r^2}\rho(r,R)$$

3.4 General Scheme of calculation for a three-electron system

Consider the Dirac-Fock type equations for a three-electron system $1s^2nlj$. Formally they fall into one-electron Dirac equations for the orbitals $1s$ 1s and nlj with the potential:

$$V(r)=2V(r|1s)+V(r|nlj)+V_{ex}(r)+V(r|R) \tag{3.12}$$

$V(r|R)$ includes the electrical and the polarization potentials of the nucleus; the components of the Hartree potential:

$$V(r|i)=\frac{1}{Z}\int d\vec{r}'\rho(r|i)/|\vec{r}-\vec{r}'| \tag{3.13}$$

$\rho(r|i)$ is the distribution of the electron density in the state | i >, V_{ex} is the exchange inter-electron interaction. The main exchange effect will be taken into account if in the equation for the $1s$ orbital we assume

$$V(r)=V(r|1s)+V(r|nlj) \tag{3.14}$$

and in the equation for the nlj orbital

$$V(r)=2V(r|1s) \tag{3.15}$$

The rest of the exchange and correlation effects will be taken into account in the first two orders of the PT by the total inter-electron interaction [13-17].

Refinement resulting from second iteration (by evaluations) does not exceed correlation corrections of the higher orders omitted in the present calculation. The relativistic potential of core (the "screening" potential)

$$2V^{(1)}(r|1s) = V_{scr}$$

has correct asymptotic at zero and in the infinity; at $\alpha \to 0$ it changes to an appropriate potential constructed on the basis of non-relativistic hydrogen-like functions.

3.5 Calculation of the self-energy part of the Lamb shift and vacuum polarization correction

Procedure for an account of the radiative QED corrections is in details given in the refs. [12,16,17]. Rergartding the vacuum polariation effect let us note that this effect is usually taken into account in the first PT theory order by means of the Uehling potential. This potential is usually written as follows (c.f.[1,11]):

$$U(r) = -\frac{2\alpha}{3\pi r}\int_1^\infty dt \exp\left(-2rt/\alpha Z\right)\left(1+1/2t^2\right)\frac{\sqrt{t^2-1}}{t^2} \equiv -\frac{2\alpha}{3\pi r}C(g), \qquad (3.16)$$

where $g = \frac{r}{\alpha Z}$. In our calculation we usually use more exact approach. The Uehling potential, determined as a quadrature (16) may be approximated with high precision by a simple analytical function. The use of new approximation of the Uehling potential permits one to decrease the calculation errors for this term down to 0.5 – 1%.

Besides, using such a simple analytical function form for approximating the Uehling potential allows its easy inclusion into the general system of differential equations. This system includes also the Dirac equations and the equations for matrix elements.

A method for calculation of the self-energy part of the Lamb shift is based on an idea by Ivanov-Ivanova (c.f.[32,37]). In an atomic system the radiative shift and the relativistic part of the energy are, in. principle, determined by one and the same physical field.

It may be supposed that there exists some universal function that connects the self -energy correction and the relativistic energy. The self-energy correction for the states of a hydrogen-like ion was presented by Mohr [1] as:

$$E_{SE}\left(H|Z,nlj\right)=0.027148\frac{Z^4}{n^3}F\left(H|Z,nlj\right) \tag{3.17}$$

The values of F are given at $Z=10-110,\ nlj=1s,2s,2p_{1/2},2p_{3/2}$.

These results are modified here for the states *1s*^{2} *nlj* of Li-like ions. It is supposed that for any ion with *nlj* electron over the core of closed shells the sought value may be presented in the form:

$$E_{SE}\left(Z,nlj\right)=0.027148\frac{\xi^4}{n^3}f\left(\xi,nlj\right)\left(cm^{-1}\right) \tag{3.18}$$

The parameter $\xi=(E_R)^{1/4}$, E_R is the relativistic part of the bounding energy of the outer electron; the universal function $f(\xi,nlj)$ does not depend on the composition of the closed shells and the actual potential of the nucleus. The procedure of generalization for a case of Li-like ions with the finite nucleus consists of the following steps [17]:

1). Calculation of the values E_R and ξ for the states *nlj* of H-like ions with the point nucleus (in accordance with the Zommerfeld formula);

2). Construction of an approximating function $f(\xi,nlj)$ by the found reference *Z* and the appropriate $F\left(H|Z,nlj\right)$ [1,11];

3). Calculation of E_R and ξ for the states *nlj* of *Li*-like ions with the finite nucleus;

4). Calculation of E_{SE} for the sought states by the formula (18).

The energies of the states of Li-like ions were calculated twice: with a conventional constant of the fine structure $\alpha = 1/137$ and with $\tilde{\alpha} = \alpha/1000$. The results of latter calculations were considered as non-relativistic. This permitted isolation of E_R and ξ. A detailed evaluation of their accuracy may be made only after a complete calculation of $E^n_{SE}(Li\,Z, nlj)$. It may be stated that the above extrapolation method is more justified than using the widely spread expansions by the parameter αZ.

3.6 Definition of the hyperfine structure parameters

Energies of the quadruple (W_q) and magnetic dipole (W_μ) interactions, which define a hyperfine structure, are calculated as follows [2,38]:

$$W_q=[\Delta+C(C+1)]B,$$

$$W_\mu=0{,}5\ AC,$$

$$\Delta=-(4/3)(4\chi-1)(I+1)/[i(I-1)(2I-1)],$$

$$C=F(F+1)-J(J+1)-I(I+1). \tag{3.19}$$

Here I is a spin of nucleus, F is a full momentum of system, J is a full electron momentum. Constants of the hyperfine splitting are expressed through the standard radial integrals:

$$A=\{[(4{,}32587)10^{-4}Z^2\chi g_I]/(4\chi^2-1)\}(RA)_{-2},$$

$$B=\{7.2878\ 10^{-7}\ Z^3Q/[(4\chi^2-1)I(I-1)\}\ (RA)_{-3}, \tag{3.20}$$

Here g_I is the Lande factor, Q is a quadruple momentum of nucleus (in Barn); radial integrals are defined as follows:

$$(RA)_{-2},=\int_0^\infty drr^2F(r)G(r)U(1/r^2,R),$$

$$(RA)_{-3}, = \int_0^\infty drr^2 [F^2(r) + G^2(r) U(1/r^2, R), \qquad (3.21)$$

and calculated in the Coulomb units (=3,57 $10^{20}Z^2$m^{-2}; = 6,174 $10^{30}Z^3$m^{-3} for valuables of the corresponding dimension).

The radial parts *F* and *G* of two components of the Dirac function for electron, which moves in the potential $V(r,R)+U(r,R)$, are determined by solution of the Dirac equations (see above; system (1)). For calculation of potentials of the hyperfine interaction $U(1/r^n,R)$, wone could use the method of differential equations by Ivanova-Ivanov [32,37].

The electric quadrupole spectroscopic HFS constant *B* of an atomic state related to the electric field gradient *q* and to electric quadrupole moment *eQ* of the nucleus as:

$$B=eqQ/h.$$

So, to obtain the corresponding value of *Q* one must combine the HFS constants data with the electric field gradient obtained in our approach from the QED PT calculation.

The details of calculation are presented in [11,14, 17,18].

3.7 Results of calculation and conclusion

3.7.1 Atom of hydrogen and superheavy H-like ion with Z=170

We have carried out the test calculation of the hyperdine structure parameters (plus deriviatives of the energy contribution on nuclear radius) for atom of hydrogen ^{1}H and superheavy H-like ion with nuclear charge Z=170. For hydrohen atom there are available sufficiently eact data for hyperfine splitting energiesof 1s, 2s levels.

For superheavy ion Z=170 there is noe experiment and we an only compair theoretical results with the fermi function for charge distribution in a nucleus with data of analogous calculation with the gauss function for charge distribution. The electron moves in the nuclear V plus vacuum-polarization potential (the core potential is naturally absent). In table 1 we present the experimental [21] an theoretical (our test calculation) results for hyperfine splitting energies for 1s, 2s levels of hydrogen atom There is very good agreement between theiry and experiment.

Table 3.1

Experimental [41] an theoretical (our test calculation) results for hyperfine splitting energies for 1s, 2s levels of hydrogen atom

Electron term Quantum numbers of total moment	Experiment $\Delta\nu(F,F')$, MHz $\Delta E(F,F')$, 10^{-3} cm^{-1}	Наш расчет $\Delta\nu(F,F')$, MHz $\Delta E(F,F')$, 10^{-3} cm^{-1}
1s $^2S_{1/2}$ (1,0)	1420,406 47, 379	1419,685 47, 355
2s $^2S_{1/2}$ (1,0)	177,557 5, 923	177,480 5, 920

In table 3.2 we present the results of our calculation for the hyperdine structure parameters (plus deriviatives of the energy contribution on nuclear radius) for the superheavy H-like ion with nuclear charge Z=170. We have used the denotations as follows:

$$A=10^8 A/Z^3 g_I, (eV);$$

$$DA=(10^{-2}/Z^4 g_I)(\partial A/\partial R), (eV/cm);$$

$$B=(10^7 BI(2I-1))/Z^3 Q, (eV/Barn);$$

$$DB=[(10^{-3} I(2I-1))/Z^4 Q](\partial B/\partial R), (eV/Barn\ cm); \qquad (3.22)$$

$$U=-(10^4/Z^4)<U(r,R)>, (eV);$$

$$DU=(10^{-1}/Z^5)(\partial <U(r,R)>/\partial R), (eV/cm);.$$

$$DV=[10^{-8}/Z^3](\partial <V>/\partial R), (eV/cm);$$

Table 3.2

Characteristics of one-electron states for H-like ion with nuclear charge Z=170 (our calculation)

	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
A	4337	831	3867	1,59	207	322	0,615
DA	1039	228	941	0,0001	56,8	84,0	0,0001
B	9091	1897	8067	0,07	475	707	0,04
DB	7245	1557	6405	0,0008	395	574	0,0003
DV	1255	273	1108	0,0011	67,7	98,3	0,0005
U	1453	282	1301	1,31	69,3	109	0,62
DU	2343	503	2071	0,0015	127	185	0,0007

3.7.2 Li-like multicharged ions

The detailled results of calculation of different energy contributions (eV) into energy of the $2s_{1/2}$-$2p_{1/2}$ transition in spectrun of the U^{89+}, calculated within different theoretical schemes: our approach (column F), MCDF (Cheng-Kim-Desclaux; A); model PT with the Dirac-Fock “0” approximation (Ivanov etal; B); relativistic multiparticle PT with the zeroth Hartree-Fock-Slater potential (Persson-Lindgren-Salomonson; C); multiparticle PT with Dirac-Fock “0” approximation (Blundell; D) have been presented in refs. [2,31-38]. Though agreement between all theoretical and experimental data is in a whole quite good, more exact results are obtained by meqans of the methods (C) and (F).

The results of our calculation for contributions to energy due to the the self-energy (SE) part of the Lamb shift and vacuum polarization correction (VP) of the Lamb shift for Li-like ions (account from core $1s^2$ energy) are also presented in ref. [38].

The detailed analysis of the VP and SE energy contributions shows that for ions with small Z the QED effects contribution is not significant, but with growth of Z (Z>40) a contribution of the QED became very important. Moreover for heavy and superheavy ions its account is principally important. Regarding the role of the nuclear finite size effect, let us underline that for multicharged ions with z<20 its contribution is very small, but for ions wit *Z*>70 it can approximately be equal to the vacuum polarization contribution on absolute value. In table 3.3 the results of calculation of the nuclear correction into energy of the low transitions for Li-like ions are presented. Our calculation showed also that a variation of the nuclear radius on several persents could lead to to changing the transition energies on dozens of thousands 10^3cm^{-1} There was performed the calculation of constants of the hyperfine interaction: the electric quadruple constant *B*, the magnetic dipole constant A with inclusion of nuclear finiteness and the Uehling potential for Li-like ions. Analogous calculations of the constant A for *ns* states of hydrogen-, lithium- and sodium-like ions were made in ref. [31-38]. In these papers other basis's of the relativistic orbitals were used. Besides, another model for the charge distribution in the nucleus was accepted and another method of numerical calculation for the Uehling potential was used. In table 3.4 the calculation results for the constants of the hyperfine splitting for the lowest excited states of Li-like ions are presented (see ref. [12]).

Table 3.3

Results calculation of the nuclear finite size correction into energy (cm^{-1}) of the low transitions for Li-like ions and values of the effective radius of nucleus (10^{-13} cm)

Z	$2s_{1/2} - 2p_{1/2}$	$2s_{1/2} - 2p_{3/2}$	R
20	- 15,1	- 15,5	3,26
30	- 117,5	- 118,0	3,73
41	- 659,0	- 670,0	4,14
59	- 6 610,0	- 6 845,0	4,68
69	- 20 690,0	- 21 712,0	4,93
79	- 62 315,0	- 66 931,0	5,15
92	- 267 325,0	- 288 312,0	5,42

Table 3.4

Constants of the hyperfine electron-nuclear interaction: A=$Z^3 g_I\ \bar{A}$ cm^{-1},

$$B=\frac{Z^3 Q}{I(2I-1)}\bar{B}\ \text{cm}^{-1}$$

nlj	Z	20	69	79	92
$2s$	$\bar{A}$	93 –03	176 -02	215 -02	314 -02
$3s$	$\bar{A}$	26 –03	51 –03	63 –03	90 –03
$4s$	$\bar{A}$	15 –03	19 –03	24 –03	36 –03
$2p_{1/2}$	$\bar{A}$	25 –03	56 –03	71 –03	105 –02
$3p_{1/2}$	$\bar{A}$	81 –04	16 –03	20 –03	31 –03
$4p_{1/2}$	$\bar{A}$	32 –04	72 –04	91 –04	11 –03
$2p_{3/2}$	$\bar{A}$	50 –04	67 –04	71 –04	72 –04
	$\bar{B}$	9 –04	13 –04	15 –04	17 –04
$3p_{3/2}$	$\bar{A}$	13 –04	19 –04	21 –04	22 –04
	$\bar{B}$	31 –05	51 –05	55–05	62 –05
$4p_{3/2}$	$\bar{A}$	62 –05	89 –05	92 –05	8 –04
	$\bar{B}$	10 –05	20 –05	22 –05	26 –05
$3d_{3/2}$	$\bar{A}$	88 –05	10 –04	11 –04	12 –04

	$\overline{B}$	51 –06	9 –05	10 –05	11 –05
$4d_{3/2}$	$\overline{A}$	35 –05	51 –05	55 –05	58 –05
	$\overline{B}$	12 –06	44 –06	50 –06	56 –06
$3d_{5/2}$	$\overline{A}$	36 –05	48 –05	50 –05	52 –05
	$\overline{B}$	21 –06	38 –06	39 –06	40 –06
$4d_{5/2}$	$\overline{A}$	15 –05	19 –05	20 –05	21 –05
	$\overline{B}$	59 –07	15 –06	16 –06	17 –06

Chapter 4

OPTIMIZED RELATIVISTIC PERTURBATION THEORY TO CALCULATING THE HYPERFINE LINE SHIFT AND BROADENING FOR HEAVY ATOMS IN THE BUFFER GAS

4.1 Introduction

Here a consistent relativistic approach, based on the atomic gauge-invariant relativistic perturbation theory and the exchange perturbation theory, is presented and applied to calculating the interatomic potentials, van der Waals constants, hyperfine structure line collision shift and broadening for heavy atoms in an atmosphere of the buffer inert gas. The corresponding data on the collision hyperfine line shift and broadening for the thallium, alkali (Rb, Cs) and lanthanide (ytterbium) atoms in an atmosphere of the inert gas (He, Kr, Xe) are listed and compared with available alternative theoretical and experimental results.

The broadening and shift of atomic spectral lines by collisions with neutral atoms has been studied extensively since the very beginning of atomic physics, physics of collisions etc [1–5]. High precision data on the collisional shift and broadening of the hyperfine structure lines of heavy elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of the buffer (for example, inert) gases are of a great interest for modern quantum chemistry, atomic and molecular spectroscopy, astrophysics and metrology as well as for studying a role of weak interactions in atomic optics and heavy-elements chemistry [1-10]. As a rule, the cited spectral lines shift and broadening due to a collision of the emitting atoms with the buffer atoms are very sensitive to a kind of the intermolecular interaction. It means that these studies provide insight into the nature of interatomic forces and, hence, they provide an excellent test of theory.

An accurate analysis of the spectral line profiles is a powerful technique for studying atomic and molecular interactions and is often necessary for probing matter in extreme conditions, such as in stellar atmospheres, ultracold traps and Bose–Einstein condensates [3,6].

Besides, calculation of the hyperfine structure line shift and broadening allows to check a quality of the wave functions (orbitals) and study a contribution of the relativistic and correlation effects to the energetic and spectral characteristics of the two-center (multi-center) atomic systems.

From the applied point of view, the mentioned physical effects form a basis for creating an atomic quantum measure of frequency [10,12,14]. The corresponding phenomenon for the thallium atom has attracted a special attention because of the possibility to create the thallium quantum frequency measure. Alexandrov et al [10] have realized the optical pumping thallium atoms on the line of 21GHz, which corresponds to transition between the components of hyperfine structure for the Tl ground state. These authors have measured the collisional shift of this hyperfine line in the atmosphere of the He buffer gas.

The detailed non-relativistic theory of collisional shift and broadening the hyperfine structure lines for simple elements (such as light alkali elements etc.) was developed by many authors (see, for example, Refs. [1-14]). However, until now an accuracy of the corresponding available data has not been fully adequate to predict or identify transitions within accuracy as required for many applications.

It is obvious that correct taking into account the relativistic and correlation effects is absolutely necessary in order to obtain sufficiently adequate description of spectroscopy of the heavy atoms in an atmosphere of the buffer gases. This stimulated our current investigation whose goals were to propose a new relativistic perturbation theory approach to calculating the interatomic potentials and hyperfine structure line collision shifts and broadening for the alkali and lanthanide atoms in an atmosphere of the inert gases. The basic expressions for the collision shift and broadening hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [6,7,11,12].

The exchange perturbation theory (the modified version EL-HAV) has been used to calculate the corresponding potentials (see details in [1-5]).

Let us note that sufficiently detailed reviews of the different versions of exchange perturbation theory are presented, for example, in Refs.[1-9]. It is worth to remind about the known difficulties of the exchange perturbation theory, associated with complex structure series, which contain the overlap integrals and exchange integrals [1]. Due to the ambiguity of the expansion in the antisymmetric functions it had been built a number of different formalisms of an exchange perturbation theory.

Usually one could distinguish two groups in dependence on the zero-order approximation of the Hamiltonian. In the symmetry adapted theories the zeroth-approximation Hamiltonian is an asymmetric, but the zeroth- approximation functions have the correct symmetry. In symmetric formalisms there is constructed a symmetric zeroth-approximation Hamiltonian such as the antisymmetric function is its eigen function.

Further formally standard Rayleigh - Schrodinger perturbation theory is applied. However, this approach deals with the serious difficulties in switching to systems with a number of electrons, larger than two. In addition, the bare Hamiltonian is not hermitian.

So the symmetry adapted theories gain more spreading. In particular, speech is about versions as EL-HAV (Eisenschitz-London-Hirschfeleder- van der Avoird), MS-MA (Murrel-Shaw-Musher-Amos) and others (see details in Refs. [4,5]).

The detailed analysis of advantages and disadvantages of the exchange perturbation theory different versions had been performed by Batygin et al (see, for example, [11,12]) in studying the hyperfine structure line shift of the hydrogen atom in an atmosphere of an inert buffer gas. In our work the modified version of the EL-HAV exchange perturbation theory has been used to calculate the corresponding potentials (see details in [4]).

On fact [4] this is the Schrödinger type perturbation theory for intermolecular or interatomic interactions, using the wave operator formalism. To include all exchange effects, wavefunctions are used whose symmetry with respect to permutations of both electronic and nuclear coordinates can be prescribed arbitrarily. The interaction energy is obtained as a series in ascending powers of the interaction operator. Further van der Avoird [4] has proved that every term in this series is real and that the terms of even order are negative definite for perturbation of the ground state. It has been also verified that up to and including third order the results of this theory, if they are restricted to electron exchange only, agree exactly with those of the Eisenschitz-London theory (see other details in Refs. [1-5]).

The next important point is choice of the most reliable version of calculation for multielectron atomic field and generating the basis of atomic orbitals. In Refs. [17-30] a consistent relativistic energy approach combined with the relativistic many-body perturbation theory has been developed and applied to calculation of the energy and spectroscopic characteristics of heavy atoms and multicharged ions.

This is the relativistic many-body perturbation theory with the optimized Dirac-Fock (Dirac-Kohn-Sham) zeroth approximation and taking into account the nuclear, radiation, exchange-correlation corrections. It is worth to remind that this approach has been successfully used to calculate the β-decay parameters for a number of allowed (super allowed) transitions and study the chemical bond effect on β-decay parameters [29]. This approach has been used in our work to generate a basis of relativistic orbiltals for heavy atoms.

Besides, the correct procedures of accounting for the many-body exchange-correlation effects and relativistic orbital basis optimization (in order to provide a performance of the gauge-invariant principle) as well as accounting for the highly excited and continuum states have been used.

Earlier it was shown [21-30] that an adequate description of the energy and spectral characteristics of the multi-electron atomic systems requires using the optimized basis of wave functions.

In Ref. [34] a new ab initio optimization procedure for construction of the optimized basis had been proposed and based on the principle of minimization of the gauge dependent multielectron contribution $Im\delta E_{ninv}$ of the lowest QED perturbation theory corrections to the radiation widths of atomic levels. The minimization of the functional $Im\delta E_{ninv}$ leads to the Dirac-Kohn-Sham-like equations for the electron density that are numerically solved. This procedure has been implemented into our approach.

In result, the numerical data on the hyperfine line collision shifts and broadening for some alkali (Rb, Cs), thallium and ytterbium atoms in atmosphere of the inert gas (such as He, Ke, Xe) are presented and compared with available theoretical and experimental data (see, detailes, for example, in [1-12]).

Besides, new data on the van der Waals constavts and other parameters for the studied two-atomic systems are presented too.

4.2 Optimized atomic perturbation theory and advanced kinetic theory of spectral lines

In order to calculate a collision shift of the hyperfine structure spectral lines one can use the following expression known in the kinetic theory of spectral lines shape (see Refs. [6,7,11,12]):

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT}\int_0^\infty [1+g(R)]dw(R)\exp(-U(R)/kT)R^2 dR, \tag{4.1a}$$

$$g(R) = \begin{cases} \dfrac{2}{3\sqrt{\pi}}\left(-\dfrac{U(R)}{kT}\right)^{3/2}, & U<0, \\ 0, & U>0, \end{cases} \tag{4.1b}$$

Here $U(R)$ is an effective potential of interatomic interaction, which has the central symmetry in a case of the systems A—B (in our case, for example, A=Rb,Cs; B=He); T is a temperature, w_0 is a frequency of the hyperfine structure transition in an isolated active atom; $d\omega(R)=Dw(R)/w_0$ is a relative local shift of the hyperfine structure line; $(1+g(R))$ is a temperature form-factor. The local shift is caused due to the disposition of the active atoms (say, the alkali atom and helium He) at the distance R. In order to calculate an effective potential of the interatomic interaction further we use the exchange perturbation theory formalism (the modified version EL-HAV) [9]).

Since we are interested by the alkali (this atom can be treated as a one-quasiparticle systems, i.e. an atomic system with a single valence electron above a core of the closed shells) and the rare-earth atoms (here speech is about an one-, two- or even three-quasiparticle system), we use the classical model for their consideration. The interaction of alkali (A) atoms with a buffer (B) gas atom is treated in the adiabatic approximation and the approximation of the rigid cores. Here it is worth to remind very successful model potential simulations of the studied systems (see, for example, Refs. [32-41]).

In the hyperfine interaction Hamiltonian one should formally consider as a magnetic dipole interaction of moments of the electron and the nucleus of an active atom as an electric quadrupole interaction (however, let us remind that, as a rule, the moments of nuclei of the most (buffer) inert gas isotopes equal to zero) [6].

The necessity of the strict treating relativistic effects causes using the following expression for a hyperfine interaction operator H_{HF} (see, eg., [1,5]):

$$H_{\mathrm{HF}} = a\sum_{i=1}^{N} I\,\frac{\alpha_i \times r_i}{r_i^3}\,, \tag{4.2}$$

$$a = -2\mu\frac{e^2 h}{2m_p c}\,,$$

where I – the operator of the nuclear spin active atom, α_i – Dirac matrices, m_p – proton mass, μ - moment of the nucleus of the active atom, expressed in the nuclear Bohr magnetons.

Of course, the summation in (4.2) is over all states of the electrons of the system, not belonging to the cores. The introduced model of consideration of the active atoms is important to describe an effective interatomic interaction potential (an active atom – an passive atom), which is centrally symmetric ($J_A = {}^1/_2$) in our case (the interaction of an alkali atom with an inert gas atom).

Let us underline that such an approximation is also acceptable in the case system “thallium atom – an inert gas atom” and some rare-earth atoms, in spite of the presence of p-electrons in the thallium (in the case of rare-earth atoms, the situation is more complicated).

Next, in order to determine a local shift within the consistent theory it should be used the expression obtained in one of versions of the exchange perturbation theory, in particular, EL-HAV version (see [1-5,8,9]). The relative local shift of the hyperfine structure line is defined with up to the second order in the potential V of the Coulomb interaction of the valence electrons and the cores of atoms as follows:

$$\delta\omega(R) = \frac{S_0}{1-S_0} + \Omega_1 + \Omega_2 - \frac{C_6}{R^6}\left(\frac{2}{\overline{E}_a} + \frac{1}{\overline{E}_a + \overline{E}_B}\right), \qquad (4.3a)$$

$$\overline{E}_{\alpha,b} = \left(I_{a,\,b} + E_{1a,\,b}\right)/2\,. \qquad (4.3b)$$

Here S_0 is the overlapping integral; C_6 is the van der Waals coefficient; I is the potential of ionization; $E_{1a,b}$ is the energy of excitation to the first (low-lying) level of the corresponding atom. The values Ω_1, Ω_2 in Eq. (4.3a) are the first order non-exchange and exchange non-perturbation sums correspondingly. These values are defined as follows:

$$\Omega_1 = \frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle \Phi_0'(1)\left|H_{HF}'\right|\Phi_k'(1)\rangle V_{k0}}{E_0 - E_k} \qquad (4.4a)$$

$$\Omega_2 = \frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle \Phi_0'(1)\left|H_{HF}'\right|\Phi_k'(1)\rangle U_{k0}}{E_0 - E_k} \qquad (4.4b)$$

$$\rho_0 = <\Phi_0^1(1)\left|H_{HF}'\right|\Phi_0'(1)\rangle / <\Phi_0^1(1)\left|\Phi_0'(1)\right\rangle$$

where $H'_{HF} = \frac{[a \times r_1]_z}{r_1^3}$ is the transformed operator of the hyperfine interaction; $[a \times r_1]_z$ is Z component of the vector product; Z - quantization axis directed along the axis of the quasi-molecule; N is the total number of electrons, which are taken into account in the calculation; E_k, $\Phi'_k(1) = F'_{k_a}(1)\varphi_{k_b}(2 \ldots N)$ are an energy and a non-symmetrized wave function of state $k = \{k_a,, k_b\}$ for the isolated atoms A and B.

The non-exchange matrix element of the Coulomb interatomic interaction is as:

$$V_{ko} = < \Phi'_k (1) \ | V(1) \,|\, \Phi'_0 (1)>. \tag{4.5a}$$

Correspondingly the exchange matrix element is as follows:

$$U_{k0} = \sum_{i=2}^{N} \langle \Phi'_k(1) |V(i)| \Phi'_0(i) \rangle \tag{4.5b}$$

The operator $V(i)$ (for example, in a case of the system Rb(a)-He(b)) can be presented as follows:

$$V(i) = U_{SCF}(r_{a3}) + U_{SCF}(r_{a4}) - 2U_{SCF}(R) + \frac{1}{r_{bi}}, \tag{4.6}$$

where $U_{SCF}(r)$ is the self-conjunctive field, created by an active atom core. The useful expressions for approximating the interaction potential and shift are presented in Refs. [11,12]:

$$U_{\text{A-B}}(R) = U^{ex}_{A-B} - C_6 / R^6, \tag{4.7}$$

$$\delta\omega^{(1)}_{\text{A-B}}(R) = \frac{2}{N\rho_0}(\chi^{1/2}(R) - \chi^{1/2}_{00})U^{\textit{обм}}_{\text{A-B}}(R) + (\Omega_1^{3/2} + \Omega_2^{3/2})_{\text{A-He}} \sqrt{\frac{S_{\text{0A-B}}}{\text{S}_{\text{0A-He}}}}, \tag{4.8}$$

where the overlap integrals $\text{S}_{\text{0A-B}}$ are determined by the standard expressions, and the potential $U^{\text{ex}}_{\text{A-B}}$ is calculated in the framework of the exchange perturbation theory [12]:

$$U^{ex} = (V_{00} - U_{00})/(1 - S_0). \tag{4.9}$$

It should also be noted that as a rule, in the alternative non-relativistic theories of [6-9] the commutator technique [11] is used when calculating the sums of the type (4). Earlier the reason of using actually approximate non-relativistic methods was the lack of reliable information on the wave functions of the excited states of the complex atoms.

Starting approximations in alternative theories [11,12] were rather simple approximations for the electronic wave functions of both active and passive atoms. In particular, in Refs. [11] the electronic wave functions were approximated by simple Slater expression (the approximation of the effective charge = Z-approximation) or simple analytical approximation formulas by Löwdin (L- approximation) and Clementi-Roothaan (C - approximation) [42] in studying the shift and broadening the hyperfine lines for such atoms as He , Rb, Cs etc.

In Refs. [12] the wave functions have been determined within the Dirac-Fock approximation, however, these authors have used the approximate non-relativistic expressions to describe the corresponding interatomic interaction potential. Besides, determination of the polarizabilities and the van der Waals constants has been performed with using the following London’s expressions [6,12]:

$$C_6^{I} = \frac{3}{2}\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}\frac{I_{\mathrm{A}}I_{\mathrm{B}}}{\mathrm{I}_{\mathrm{A}}+I_{\mathrm{B}}}, \tag{4.10a}$$

$$C_6^{\mathrm{II}} = \frac{3}{2}\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}\frac{1}{\sqrt{\frac{\alpha_{\mathrm{A}}}{\mathrm{n}_{\mathrm{A}}}}+\sqrt{\frac{\alpha_{\mathrm{B}}}{\mathrm{n}_{\mathrm{B}}}}}, \tag{4.10b}$$

$$C_6^{III} = \frac{3}{2}\alpha_B I_B\sum_k \frac{f_{ko}}{(E_o - E_k)(E_o - E_k + I_B)}. \tag{4.10c}$$

where f is the oscillator strength, other notations are the standard. However, sufficiently large error in definition of the van der Waals constants could provide a low accuracy of calculating the interatomic potentials. It is worth to note that the authors of the cited works indicate on the sufficiently large error (~ 50%) in the calculation of the collision shifts.

Let us return to consideration of the van der Waals coefficient C_6 for the interatomic *A-B* interaction. The van der Waals coefficient may be written as [13,43,44]:

$$C_6(L,M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)} \cdot \mathrm{C}_{6,2}(\mathrm{l}) \quad , \tag{4.11}$$

where $C_{6,0}$ *(L)* is the isotropic component of the interaction and $C_{6,2}$ *(L)* is the component corresponding to the $P_2(cos\theta)$ term in the expansion of the interaction in Legendre polynomials, where the angle specifies the orientation in the space-fixed frame.

The dispersion coefficients $C_{6,0}$ *(L)* and $C_{6,2}$ *(L)* may be expressed in terms of the scalar and tensor polarizabilities $\alpha_0(L;iw)$ and $\alpha_2(L;iw)$ evaluated at imaginary frequencies [13]. In particular, one may write in the helium case as follows:

$$C_{6,0}(L) = \frac{3}{\pi} \cdot \int_0^\infty \alpha_0(L;iw)\bar{\alpha}_{He}(iw)dw, \tag{4.12}$$

where $\bar{\alpha}_{He}$ is the dynamic polarizability of He.

The polarizabilities at imaginary frequencies are defined in atomic units by the following formula:

$$\alpha_{||}(L,M;iw) = 2\sum_{\gamma,M_\gamma} \frac{(E_\gamma - E_L)|<LM|\hat{z}|L_\gamma M_\gamma>|^2}{(E_\gamma - E_L)^2 + w^2} \tag{4.13}$$

where E_γ is the energy of the electronically excited state $|L_\gamma M_\gamma>$ and the *z* axis lies along the internuclear axis.

Obviously, generally speaking, the calculation of the dynamic polarizability and the resulting van der Waals constants is connected with a summation over infinite number of intermediate states (the states of the discrete spectrum and integrating over the states of the continuous spectrum).

This is a known problem, which greatly complicates the computational procedure and significantly reduces an accuracy of the computing the atomic characteristics.

On the other hand, it is known that the space of functions of the atomic states can be stretched over the space of the Sturm orbitals, which is both discrete and countable [6,35,43].

Thus, it allows to eliminate a problem of accounting the continuous spectrum within the formally exact approach.

Naturally, the set of Sturm orbitals should be introduced with specially prescribed asymptotics that is crucial for the convergence of the spectral expansion, including a spectral expansion of the corresponding Green's functions.

4. 3 Relativistic many-body perturbation theory with the Kohn-Sham zeroth approximation and the Dirac-Sturm method

4.3.1 Relativistic many-body perturbation theory with the Kohn-Sham zeroth approximation

As it is well known (see also Refs. [1,7]), the non-relativistic Hartree-Fock method is mostly used for calculating the corresponding wave functions. More sophisticated approach is based on using the relativistic Dirac-Fock wave functions (first variant) [15,16]. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with the corresponding density functional, i.e within the Dirac-Kohn-Sham theory [45-48]. In fact, the theoretical models involved the use of different consistency level approximations led to results at quite considerable variance.

It is obvious that more sophisticated relativistic many-body methods should be used for correct treating relativistic, exchange-correlation and even nuclear effects in heavy atoms. (including the many-body correlation effects, intershell correlations, possibly the continuum pressure etc [21-30]). In our calculation we have used the relativistic functions, which are generated by the Dirac-Kohn-Sham Hamiltonian [18,27-30]. In a number of papers it has been rigorously shown that using the optimized basis in calculating the atomic electron density dependent properties has a decisive role. This topic is in details discussed in many Refs. (see, for example, [6,15,28-32,49]).

As usual, a multielectron atom is described by the Dirac relativistic Hamiltonian (the atomic units are used):

$$H = \sum_i h(r_i) + \sum_{i>j} V\left(r_i r_j\right). \tag{4.14}$$

Here, *h(r)* is one-particle Dirac Hamiltonian for electron in a field of the finite size nucleus and *V* is potential of the inter-electron interaction.

In order to take into account the retarding effect and magnetic interaction in the lowest order on parameter α^2 (the fine structure constant) one could write [18]:

$$V\left(r_i r_j\right) = exp\left(i\omega_{ij} r_{ij}\right) \cdot \frac{\left(1 - \alpha_i \alpha_j\right)}{r_{ij}}, \tag{4.15a}$$

where ω_{ij} is the transition frequency; α_i ,α_j are the Dirac matrices. The Dirac equation potential includes the electric potential of a nucleus and electron shells and the exchange-correlation potentials. The standard KS exchange potential is as follows [45]:

$$V_X^{KS}(r) = -(1/\pi)[3\pi^2 \rho(r)]^{1/3}. \tag{4.15b}$$

In the local density approximation the relativistic potential is [45]:

$$V_X[\rho(r), r] = \frac{\delta E_X[\rho(r)]}{\delta \rho(r)}, \tag{4.16}$$

where $E_X[\rho(r)]$ is the exchange energy of the multielectron system corresponding to the homogeneous density $\rho(r)$, The corresponding correlation functional is [6, 28]:

$$V_C[\rho(r), r] = -0.0333 \cdot b \cdot \ln[1 + 18.3768 \cdot \rho(r)^{1/3}], \tag{4.17}$$

where *b* is the optimization parameter (for details see Refs. [6,31,32]).

As it has been underlined, an adequate description of the multielectron atom characteristics requires using the optimized basis of wave functions. In our work it has been used ab initio optimization procedure for construction of the optimized basis of the relativistic orbitals. It is reduced to minimization of the gauge dependent multielectron contribution $Im\delta E_{ninv}$ of the lowest QED perturbation theory corrections to the radiation widths of atomic levels.

The minimization of the functional $Im\delta E_{ninv}$ leads to the Dirac-Kohn Sham-like equations for the electron density that are numerically solved. According to Refs. [31], the gauge dependent multielectron contribution can be expressed as functional, which contains the multi-electron exchange-correlation ones. From the other side, using these functionals within relativistic many-body perturbation theory allows effectively to take into account the second –order atomic perturbation theory (fourth-order QED perturbation theory) corrections. In our work the corresponding functionals of Ref. [34] have been used. As a result one can get the optimal perturbation theory one-electron basis. In concrete calculations it is sufficient to use more simplified procedure, which is reduced to the functional minimization using the variation of the correlation potential parameter *b* in Eq. (4.16).

The differential equations for the radial functions *F* and *G* (components of the Dirac spinor) are:

$$\frac{\partial F}{\partial r}+\left(1+\chi\right)\frac{F}{r}-\left(\varepsilon+m-V\right)G=0,$$

$$\frac{\partial G}{\partial r}+\left(1-\chi\right)\frac{G}{r}+\left(\varepsilon-m-V\right)F=0, \tag{4.18}$$

where *F*, *G* are the large and small components respectively; χ is the quantum number.

At large χ, the functions *F* and *G* vary rapidly at the origin; so, one could have

$$F(r), G(r) \approx r^{\gamma-1},\ \gamma = \sqrt{\chi^2 - \alpha^2 z^2}\ .$$

This creates difficulties in numerical integration of the equations in the region $r \to 0$. To prevent the integration step from becoming too small it is usually convenient to turn to new functions isolating the main power dependence:

$$f = Fr^{1-|\chi|}\ ,$$

$$g = Gr^{1-|\chi|}.$$

The Dirac equations for *F* and *G* components are transformed as follows [18]:

$$f' = -(\chi + |\chi|) f / r - \alpha ZVg - (\alpha ZE_{n\chi} + 2/\alpha Z)g,$$

$$g' = (\chi - |\chi|) g / r - \alpha ZVf + \alpha ZE_{n\chi} f. \qquad (4.19)$$

Here $E_{n\chi}$ is one-electron energy without the rest energy. The boundary values are defined by the first terms of the Taylor expansion:

$$g = \left(V(0) - E_{n\chi}\right) r\alpha Z / (2\chi + 1); \quad f = 1 \text{ at } \chi < 0,$$

$$f = \left(V(0) - E_{n\chi} - 2/\alpha^2 Z^2\right)\alpha Z; \quad g = 1 \text{ at } \chi > 0. \qquad (4.20)$$

The condition $f, g \to 0$ at $r \to \infty$ determines the quantified energies of the state $E_{n\chi}$. The system of equations (4.19) is numerically solved by the Runge-Kutta method (‘Superatom’ PC package is used [17-37]). The other details can be found in Refs. [21-30].

The basic idea of the Dirac-Sturm approach is as follows [6,9,35,43]. In the usual formulation as basis functions used system of eigenfunctions of the generalized eigenvalue problem for the family of operators:

$$(H_0 - \varepsilon)\Phi_\nu = \Lambda_\nu \hat{g}\Phi_\nu , \tag{4.21}$$

where H_0 – unperturbed Hamiltonian of a system, $\hat{g}$ is a weighting operator, generally speaking, do not commute with the operator H_0; Λ_ν, Φ_ν - eigenvalues and eigenfunctions of equation (4.21).

A weighting operator in Eq. (4.21) is usually chosen so that unlike a spectrum of H_0, the spectrum of (4.21) is a purely discrete. Using the orthogonality and completeness conditions, it is easy to show that the Green operator of the unperturbed problem is diagonal in a representation, defined by a set of functions Φ_ν and the corresponding expansion is as follows:

$$G_0(\varepsilon) = \sum_\nu |\, \Phi_\nu >< \Phi_\nu \,| \,/\, \Lambda_\nu(\varepsilon) \tag{4.22}$$

and contains only a single summation over the quantum numbers $\{\nu\}$.

As the operator H_0 we use the Dirac-Kohn-Sham Hamiltonian. The corresponding Dirac-Kohn-Sham equation can be written in the next general form [9]:

$$[h_{DKS}(x) - \varepsilon_n]u_n(x) = 0 \tag{4.23}$$

Along with discrete spectrum ($\varepsilon=\varepsilon_n \le \varepsilon_F$) there is a continuous spectrum of the eigen-values ($\varepsilon > \varepsilon_F$), corresponding to the Dirac-Kohn-Sham virtual orbitals. In the Sturmian formulation of the problem one should search for the eigen-values and eigen-functions of the following equation:

$$[h_{DKS}(x) - \varepsilon]\varphi_\nu = \lambda_\nu \rho(x)\varphi_\nu \tag{4.24}$$

where

$$\varepsilon = E - \sum_{k=1}^{N-1} \varepsilon_{n_k} \tag{4.25}$$

Let us note that when $\varepsilon<0$ equation (24) has a purely discrete spectrum eigenvalues $\lambda_\nu = \lambda_\nu(\varepsilon)$.

As the weight of the operator there are commonly used operators, proportional to a part or even all potential energy in the Hamiltonian H_0. Further, it is easily to understand that the Fourier-image of the one-particle Green's function in the Dirac-Kohn-Sham approximation can be represented as an expansion on the eigenfunctions of (24) [6,9]:

$$G^{(+)} = (x, x'; \varepsilon) = \sum_\nu \frac{\tilde{\varphi}_\nu(x)\tilde{\varphi}_\nu^*(x')}{\lambda_\nu(\varepsilon) - 1}, \tag{4.26}$$

where $\tilde{\varphi}_\nu(x)$ is the Sturm designed function:

$$\tilde{\varphi}_\nu(x) = \varphi_\nu(x) - \sum_{k=1}^{N} u_{n_k}(x) < u_{n_k} | \varphi_\nu > \tag{4.27}$$

In the case of the single-particle perturbed operator, say,

$$W(x) = \sum_{a=1}^{N} w_a(x) \tag{4.28}$$

the second-order correction to an energy of the atom is determined by the standard expression of the following type:

$$\delta E^{(2)} = -\sum_{k=1}^{N} < u_{n_k} | wG^{(+)}(\varepsilon_{n_k}) w | u_{n_k} >=$$

$$= -\sum_{k=1}^{N} \sum_\nu | < \tilde{\varphi}_\nu | w | u_{n_k} > |^2 / [\lambda_\nu(\varepsilon_{n_k}) - 1] \tag{4.29}$$

and it actually contains only the summation over the occupied states (core) and virtual orbitals of the Dirac-Kohn-Sham-Sturm type relating to a purely discrete spectrum.

If the operator $w_a(x)$ is an interaction with an external electric field, the expression (29) determines the many-electron atom polarizability in the relativistic Dirac-Kohn-Sham approximation.

Let us illustrate the specific numerical implementation of relativistic method of the Sturm expansions on the example of the rubidium atom. Calculation of the static polarizability is actually reduced to two stages. In the first stage one should solve the system of relativistic Dirac-Kohn-Sham equations with respect to the Dirac radial functions and the Lagrange diagonal parameters ε^{5s},ε^{4p}, ε^{4s} etc.

In the second stage of the calculation procedure the system of equations equivalent to (24) is solved numerically:

$$(-i\alpha c\nabla + V_N(r) + \delta_i V_C(r) + V_X(r\,|\,b_i) - \varepsilon_i)\varphi_i = 0\,, \qquad (4.30)$$

where, as above, V_N is the potential of the electron-nuclear interaction, V_C is a mean-field potential generated by the other electrons; V_X is the Kohn-Sham potential.

Two parameters ε_i , δ_i correspond to each orbital “i” of a real or Sturmian state. The parameter δ_i =1 for orbitals of the real states. It is also important to emphasize that all orbitals of the Sturmian supplement of the Eq. (4.26) have an exponential asymptotic behavior as $r\to\infty$, which coincides with the asymptotic behavior of the last real state orbitals in the corresponding basis of the real state orbitals. In each case, the functions of the accounted real states represent a reduced spectral expansion of the Green's function G.

The residual part decreases as $\exp[-r(-2\varepsilon)^{1/2}]$ for $r\to\infty$ (here ε is the eigen energy of the explicitly accounted last real state). All orbitals of the Sturm supplement have absolutely the same asymptotic in the corresponding basis. This fact is very significant in terms of convergence of the method.

As usually, the number of explicitly accounted real state functions is determined by the concrete numerical application of the method to computing the studied atomic characteristics. Other details can be found, for example, in Refs. [6,9,35].

4.4 Shift and broadening of the hyperfine spectral line for multielectron atoms in an atmosphere of the buffer gas

4.4.1 Shift and broadening of the thallium and ytterbium hyperfine line in an atmosphere of the inert gas

At first, let us consider the thallium atom in atmosphere of the inert gas. Its studying is of a great interest as this atom a sufficiently heavy. In contrast to more simple alkali atoms (look below) the thallium atom contains p-electrons outside closed shells and has a nuclear charge Z = 81. Obviously, a correct treating relativistic and exchange-correlation effects is critically important for accurate describing its energy and spectral characteristics.

In Table 4.1 the theoretical values of the van der Waals constants (in atomic units) respectively, for atom Tl (Tl - He, Kr, Xe) are listed. There are presented our results (*) obtained from our relativistic calculation by the optimized Dirac-Kohn-Sham method combined with the Dirac-Sturm approach, the calculation results by Batygin et al, based on the approximation formulas (4.10a)-(4.10c), the Hartree-Fock data by Penkin et al, as well as experimental data (from refs. [8,9,10-13]).

Table 4.1

Theoretical values of the van der Waals constants (in atomic units) respectively, for atom Tl (Tl - He, Kr, Xe); see explanations in the text.

	TI – He	TI – Ar	TI- Kr	TI- Xe
C_6^I (10a)	17.5	129	180	291
C_6^{II} (10b)	20.5	148	212	318
C_6^{III} (10c)	20.33	133	193	296
C_6 (Hartree-Fock)	6.59	48	71	111
C_6 (our data ^{a})*	12.1	106	157	265
C_6 (our data^{b})*	14.5	119	173	289
C_6 (experiment)	-	100	150	260

Note:[a] – calculation with optimization[*]; [b] – calculation without optimization;
In Table 4.2 there are listed the results of our calculation of the interatomic interaction potential U (R) and the values of the local shift $\delta\omega$ (R) (all values are in atomic units) of the thallium hyperfine spectral line for different values of the internuclear distance in the system TI - He. For comparison, similar results of the calculation of the potential U (R) and the local shift $\delta\omega$ (R) with using the single-configuration Dirac-Fock method [12] are presented too.

It is noteworthy sufficiently large error for values of the van der Waals constants, obtained during calculating on the basis of formula (4.10), as well as within the standard Hartree-Fock method.

The calculation shows the importance of the quality of the atomic wave functions (using an optimization and correct account for the exchange-correlation effects and continuum “pressure” etc.) for an adequate description of the corresponding constants.

Table 4.2

Local shift and interatomic interaction potential (in atomic units) for the pair TI - He.

	Dirac-Fock method		Our theory [8,9]	
R	$\delta\omega(R) \bullet$	$U(R) \cdot 10^3$	$\delta\omega(R) \bullet 10^2$	$U(R) \cdot 10^3$
5	4.22	7.6	3,92	6.93
6	1.34	2.0	1,21	1.76
7	0.329	0.44	0.27	0.38
8	0.0788	0.099	0.070	0.085
9	0.0032	0.024	0.0025	0.020
10	-0.0145	-0.076	-0.0131	- 0.067
11			- 0.0119	-0.008

In Table 4.3 we list the results of our calculation (as all values are given in atomic units) interatomic interaction potential *U (R)* and the values of the local shift $\delta\omega$ (R) for pairs TI-Kr, TI-Xe.

Table 4.3

Local shift and interatomic interaction potential (in atomic units) for the pair TI – Kr, Xe (see text)

	T1-Kr (Our theory)	T1-Xe (Our theory)

R	$\delta\omega(R)$ •	$U(R) \cdot 10^3$	$\delta\omega(R)$ •	$U(R) \cdot 10^3$
5	-14.30	13.24	-19,05	18.31
6	-2.88	6.10	-8.22	5.95
7	-1.44	1.72	-2.67	2.04
8	-0.67	0.49	-1.52	0.65
9	-0.48	0.06	-0.74	0.01
10	-0.35	-0.03	-0.48	- 0.08
11	-0.24	- 0.04	- 0.37	-0.09

Further in Table 4.4 we present our theoretical values (theory C) for the thallium atom hyperfine line collisional shift at the temperature T = 700K for a number of the diatomic systems, in particular, the pairs of TI - He, TI - Kr, Tl-Xe. For comparison, in this table there are also listed the results of calculation on the basis of the single-configuration Dirac-Fock method Batygina DF et al. [12] (theory A), the optimized DF-like method [8] (theory B), as well as experimental data Choron-Scheps-Galagher (the Virginia group) . The qualitative estimate from Ref. [10] has been listed as well.

Table 4.4

The collisional shift f_ρ (in Hz/Torr) of the thallium hyperfine line for pairs TI - He, TI - Kr, Tl-Xe at T = 700^oK; Experiment and the qualitative estimate by Choron-Scheps-Galagher (Virginia group); Theory: A- single-configuration Dirac-Fock method; B – the optimized Dirac-Fock method; C- our theory (see text).

System	T1-He	T1-Kr	T1-Xe
Experiment	130 ± 30	-490±20	-1000±80
Qualitative	-	-	-5500
Theory A	155.0	-850.0	-1420.0
Theory B	139.0	-	-
Theory C	137.2	-504	-1052

In Table 4.5 we present the theoretical data on the collisional shift f_ρ (in Hz/Torr) the thallium atom hyperfine line at different temperatures (T^0K) for the systems TI - He, TI - Kr, Tl-Xe: Theory A - the single-configuration Dirac-Fock method Batygina DF et al. [12]; C- our theory [8,9].

Table 4.5 The temperature dependence of the collisional shift f_ρ (in Hz/Torr) for pairs TI - He, TI - Kr, Tl-Xe; Theory: A- single-configuration Dirac-Fock method; C- our theory;

Pair	T1—	T1—	T1—	T1—Xe
T, K	Theory	Theory	Theor	Theory
700	155	137,2	-504	-1052
750	153.0	135,3	-461	-964
800	151	134,1	-422	-899
850	149	133,3	-391	-841
900	147.5	131,4	-362	-794
950	146	129,1	-330	-751
1000	143	126,2	-308	-713

As can be seen from the presented data, our theory provides a physically reasonable agreement with experimental data on the hyperfine line collisional shifts for the pairs of TI-He, TI-Kr, Tl-Xe.

In Table 4.6 we present our calculated values for adiabatic broadening Γ_d/p (in Hz / Torr) of the thallium atom hyperfine line at different temperatures for the TI – He pair: C - our theory; A theory [12]. In Table 4.7 we list the similar our theoretical data on the thallium atom hyperfine line adiabatic broadening of Γ_d/p (in Hz / Torr) for the pairs TI - Kr, TI-Xe.

Table 4.6

Adiabatic broadening Γ_d/p (in Hz / Torr) for the TI - He:
Theory A- single-configuration Dirac-Fock method; C- our theory.

T, K	TI – He Theory A	TI – He Theory C
700	2.83	2.51
800	2.86	2.54
900	2.90	2.58
1000	2.89	2.56

Table 4.7

Adiabatic broadening Γ_a/p (in Hz / Torr) for the TI – Kr, Yl-Xe (our theory).

T, K	TI- Kr	TI- Xe
700	6.81	17.3
800	5.89	14.6
900	5.26	12.9
1000	5.24	11.5

It is easily to estimate that the ratio values (Γ_a/p) / f_p ~ 1/50 for the system TI - He, (Γ_a/p) / f_p ~ 1/70 for the system TI - Kr and (Γ_a/p) / f_p ~ 1/60 for the TI-Xe. These estimates (at first it had been noted in Ref.[12]) show that well-known in the theory of optical range spectral line broadening Foley law $\Gamma_a \sim |\Delta|$ (see, for example, [6]) is incorrect for the spectral lines of transitions between components of the hyperfine structure. At least this fact is absolutely obvious for the thallium atom.

In any case we suppose that more detailed experimental studying are to be very actual and important especially a light of availability of the theoretical data on temperature dependences of the thallium hyperfine line collisional shift and broadening. Obviously, this is also very actual from the point of view of the construction the thallium quantum frequency measure, as well as studying a role of the weak interactions in atomic physics and physics of collisions (see, for example, [6,10]).

Further we present the results of our studying hyperfine line collisional shift for alkali atoms (rubidium and caesium) in the atmosphere of the helium gas. In Table 4.8 we present our data on the van der Waals constants in the interaction potential for alkali Rb, Cs atoms with inert gas atoms Ne, Kr, Xe, and also available in the literature experimental data [10,11].

In Table 4.9 we list the results of our calculating (in atomic units) interatomic potentials, local shifts $\delta\omega(R)$ for the pair Cs-He.

Table 4.8

The van der Waals constants (in atomic units.) for alkali atoms, interacting with inert gas atoms Ne, Kr, Xe (see text).

Pair of atoms	Our theory	Experiment
Rb-He	42	41

Rb –Kr	484	470
Rb –Xe	758	-
Cs-He	52	50
Cs-Kr	582	570
Cs-Xe	905	-

Table 4.9

The interatomic potential (10^5) and local $\delta\omega(R)$ shift (10^5) for Cs-He pair (in atomic units; see text)

R	$\delta\omega(R)$	U (R)
8	4280	610
9	2845	336
10	1890	169
11	955	77
12	482	32
13	251	12.8
14	113	4.1
15	59	1.9

Noteworthy is the fact that an accuracy of the experimental data for the van der Waals constants does not exceed 10 % for heavy alkali atoms. Calculation has shown that the optimization of the relativistic orbitals basis and accounting for the exchange-correlation effects seem to be very important for obtaining adequate accuracy of the description of the constants.

In Table 4.10 and 4.11 we present our theoretical results for the hyperfine line observed shift f_p (1/Torr) in a case of the Rb-He and Cs-He pairs. The experimental and alternative theoretical results by Batygin et al [11] for f_p are listed too. At present time there are no precise experimental data for a wide interval of temperatures in the literature.

Table 4.10

The observed f_ρ (10^{-9} 1/Torr) shifts for the systems of the Cs-He and corresponding theoretical data (see text).

T, K	Experi-	Our	Theory [a]	Theory [b]	Theory [c]
223	-	178	164	142	169
323	135	137	126	109	129
423	-	123	111	96	114
523	-	112	100	85	103

623	-	105	94	78	96
723	-	98	-	-	-
823	-	92	-	-	-

Note:[a] –calculation with using the He wave functions in the Clementi-Rothaane approximation; [b] – calculation with using the He wave functions in the Z-approximation; [c] –calculation with using the He wave functions in the Löwdin approximation;

The theoretical data from Refs. [11] are obtained on the basis of calculation within the exchange perturbation theory with using the He wave functions in the Clementi-Rothaane approximation [42] (column: Theory[a]), and in the Z-approximation (column: Theory[b]), and in the Löwdin approximation (column: Theory[c]). The important feature of the developed optimized perturbation theory approach is using the optimized relativistic orbitals basis, an accurate accounting for the exchange-correlation and continuum pressure effects with using the effective functionals [18,34].

The difference between the obtained theoretical data and other alternative calculation results can be explained by using different perturbation theory schemes and different approximations for calculating the electron wave functions of heavy atoms. It is obvious that the correct account for the relativistic and exchange-correlation and continuum pressure effects will be necessary for an adequate description of the energetic and spectral properties of the heavy atoms in an atmosphere of the heavy inert gases (for example, such as Xe).

Table 4.11

The observed f_ρ (10^{-9} 1/Torr) shifts for the systems of Rb-He and corresponding theoretical data (see text).

T, K	Experi-	Our	Theory[a]	Theory b	Theory[c]
223	-	113	79	67	81
323	105	101	73	56	75
423	-	89	62	48	64
523	-	80	55	43	56
623	-	73	50	38	50
723	-	71	47	36	47

823	-	69	-	-	-

Note:[a] –calculation with using the He wave functions in the Clementi-Rothaane approximation; [b] – calculation with using the He wave functions in the Z-approximation; [c] –calculation with using the He wave functions in the Löwdin approximation;

4.5 Conclusion

In this chapter a brief review of the experimental and theoretical works on the hyperfine structure line collision shifts for heavy atoms in an atmosphere of the buffer inert gases is given. A new, consistent relativistic perturbation theory combined with the exchange perturbation theory, is presented and applied to calculating the interatomic potentials, van der Waals constants, hyperfine line collision shift and broadening for some heavy atoms in an atmosphere of the buffer inert gases. It should be noted that the presented approach can be naturally generalized in order to describe the energy and spectral characteristics of other atomic systems and buffer mediums.

The calculation results on the hyperfine line collision shift and broadening for the alkali (Rb, Cs), thallium, and ytterbium atoms in an atmosphere of the inert gas (He, Kr, Xe) are listed and compared with available alternative theoretical and experimental results. The obtained data for the (Γ_a/p) / f_p ratio allowed to confirm that the well-known Foley law $\Gamma_a \sim f_\mathrm{p}$ in the theory of optical range spectral line broadening is incorrect for the spectral lines of transitions between components of the hyperfine structure of the heavy multielectron atoms.

The studying hyperfine structure line collision shifts and widths for different heavy atomic systems in the buffer gases opens new prospects in the bridging of quantum chemistry and atomic and molecular spectroscopy and physics of collisions.

These possibilities are significantly strengthened by a modern experimental laser and other technologies [10,50-56]. Really, new experimental technologies in physics of collisions may provide a measurement of the atomic and molecular collision spectral parameters with very high accuracy.

Chapter 5

THE GREEN'S FUNCTIONS AND DENSITY UNCTIONAL APPROACH TO VIBRATIONAL STRUCTURE IN THE PHOTOELECTRON SPECTRA OF MOLECULES: REVIEW OF METHOD

5.1 Introduction

We present the basis's of the new combined theoretical approach to vibrational structure in photoelectron spectra of molecules. The approach is based on the Green's function method, which generalizes the Cederbaum-Domske formalism, and quasiparticle density functional theory. It generalizes the known Green's function approach by It is presented a new procedure for determination of the density of states, which describe the vibrational structure in molecular photoelectron spectra.

A number of phenomena, provided by interaction of electrons with vibrations of the atomic nuclei in molecules or solids under availability of of the electron states degeneration is usually called as the Jahn-Teller effect. This interaction may lead to local deformations, which are the reason of the structural phase transitions in the solids (statical Jahn-Teller effect)or appearance of the connected electron-vibrational states (a dynamical Jahn-Teller effect) [1-4]. Indeed, the physics of the interaction of electrons with vibrations of the atomic nuclei in molecules or solids is more richer (c.f.[1-111]). One could mention here a great field of the resonant collisions of electrons with molecules, which are one of the most efficient pathways for the transfer of energy from electronic to nuclear motion. While the corresponding theory has been refined over the years with sophisticated and elaborate non-local treatments of the reaction dynamics, such studies have for the most part treated the nuclear dynamics in one dimension. This situation has resulted from the fact that, as the field of electron-molecule scattering developed, both experimentally and theoretically, the phenomena of vibrational excitation and dissociative attachment were first understood for diatomics, and it seemed natural to extend that understanding to polyatomic molecules using 1-D or single-mode models of nuclear motion. However a series of experimental measurements of these phenomena in small polyatomic molecules have proven to be uninterpretable in terms of atomic motion with single degree of freedom. Reader can find more details about this topic in the recent paper by Rescigno et al [4].

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 [9-49]. Very interesting quote has been indicated by Bartlett and Musiał and earlier by Wilson: "*Ab initio quantum chemistry is an emerging computational area that is fifty years ahead of lattice gauge theory and a rich source of new ideas and new approaches to the computation of many fermion systems"* [26]. Following to ref. [26] we repeat that *d*riving these developments are the types of problems addressed by quantum chemists, as shown in Fig. 5.1. Primary among these are potential-energy surfaces (PES) which describe the behavior of the electronic energy with respect to the locations of the nuclei, subject to the underlying Born-Oppenheimer or clamped nuclei approximation. From the ground- and excited-state wave functions one could in principle obtain all properties that arise from a solution to vibrational Schrödinger equation that gives the frequencies and with derivatives of the dipole moment, the infrared intensities [26-39].

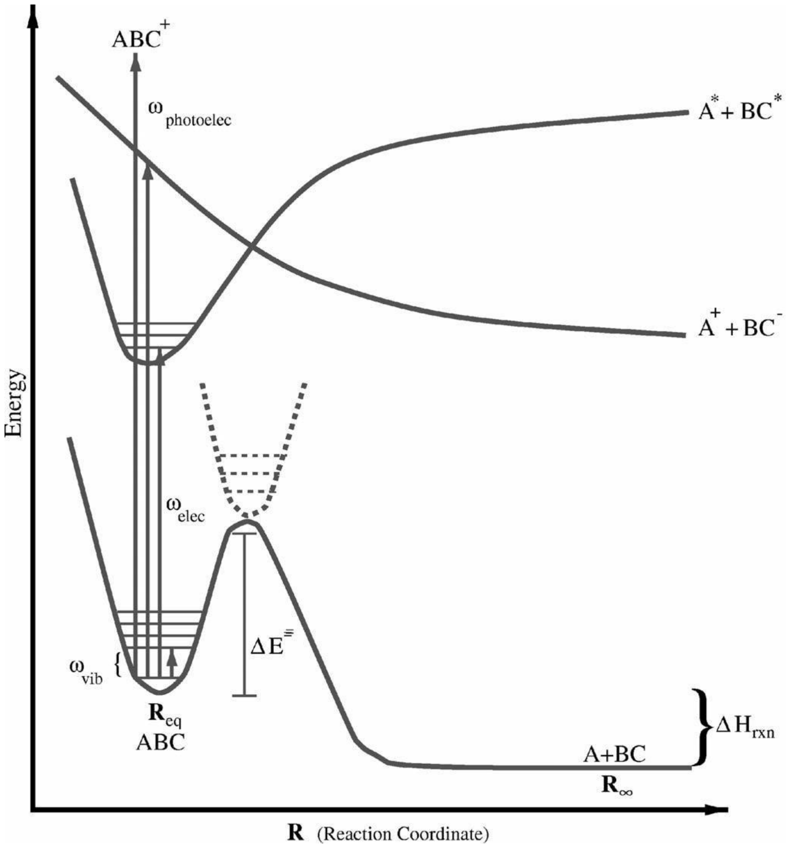

Figure 1. The nature of quantum chemical problems (from ref. [26]).

Electronic excited states are also accessible along with electronic and photo-electron spectra. The properties that arise from the one-particle density matrix, such as dipole moments, hyperfine coupling constants, and electric-field gradients, are readily available. From even higher-order electric-field derivatives, one obtains hyperpolarizabilities, which determine nonlinear optical behavior. From derivatives relative to atomic displacements in molecules, one obtains anharmonic effects on vibrational-rotational spectra. In result , one could mention that a main objective is an accurate solution of the Schrödinger equation for molecules composed of comparatively light elements.

As it is often takes a place, the old multi-body quantum theoretical approaches, which have been primarily developed in a theory of superfluity and superconductivity, and generally speaking in a theory of solids, became by the powerful tools for developing new conceptions in molecular calculations [50-65]. Many of them offers a synthesis of cluster expansions, Brueckner's summation of ladder diagrams, the summation of ring diagrams Gell-Mann and an infinite-order generalization of many-body perturbation theory MBPT (Kelly, 1969; Bartlett and Silver, 1974a, 1976. Using quantum-field methods in molecular theory allowed to obtain a very powerful approach for correlation in many-electron systems. Only with this property are applications to polymers, solids, or the electron gas possible, and, even for small molecules, its effects are numerically quite significant. Configuration interaction methods, long the focus of the correlation problem in quantum chemistry Shavitt, 1998, do not, in general, have this property which is responsible for the emphasis on the coupled cluster theory and its multi-body perturbation theory approximations (Kelly, 1969; Bartlett and Silver, 1974a, 1974b; Pople *et al.*, 1976) in chemistry. For more details, the history of coupled cluster theory is best told from the viewpoint of some of its principal developers (look review [26]).

The Green's method is very well known in a quantum theory of field, quantum electrodynamics , quantum theory of solids (c.f.[61-63]). Naturally, an attractive idea was to use it in the molecular calculations. Returning to problem of description of the vibrational structure in photoelectron spectra of molecules, it is easily understand that this approach has great perspective as it was shown by Cederbaum et al (c.f.[65-68]). One could note that the experimental photoelectron (PE) spectra usually show a pronounced vibrational structure. Many papers have been devoted to treatment of the vibrational spectra by construction of potential curves for the reference molecule (the molecule which is to be ionized) and the molecular ion.

Usually the electronic Green's function is defined for fixed position of the nuclei. As result, only vertical ionization potentials (V.I.P.'s) can be calculated [65]. The cited method, however, requires as input data the geometries, frequencies, and potential functions of the initial and final states. Since in most cases at least a part of these data are unavailable, the calculations have been carried out with the objective of determining the missing data by comparison with experiment.

Naturally, the Franck-Condon factors are functions of the derivatives of the difference between the potential curves of the initial and final states with respect to the normal coordinates. One could agree here that highly accurate calculations are necessary to obtain good results with the above methods. To avoid this difficulty and to gain additional information about the ionization process, Cederbaum et al [65-68] extended the Green's functions approach to include the vibrational effects and showed that the Green's functions method allowed the *ab initio* calculation of the intensity distribution of the vibrational lines, of the vibrational frequencies of the reference molecule and its ions, and of geometry shifts due to ionization and particle attachment. Besides, a great advancement here is connected with a possibility of the quite exact calculation of ionization potentials (I.P.'s) for molecules.

According to ref.[65], starting from Hartree-Fock (HF) calculation [71,72] the electronic Green's functions have been calculated applying a many-body perturbation expansion. In this method the Koopmans' defect, i.e., the difference between the I.P. and the value derived from the Koopmans' theorem, is calculated directly, avoiding the usual subtraction of large numbers of roughly equal magnitude.

Further let us remember that for larger molecules and solids, far more approximate but more easily applied methods such as density-functional theory

(DFT) [40-42] or from the wave-function world the simplest correlated model MBPT are preferred. Indeed, in the last decades DFT theory became by a great, quickly developing field of the modern quantum computational chemistry of atoms, molecules, solids.

Naturally, this approach does not allow to reach a spectroscopic accuracy in description of the different molecular properties, nevertheless, the key idea is very attractive and can be used in new combined theoretical approaches.

Here we present the basis's of the new combined theoretical approach to vibrational structure in photoelectron spectra of molecules. The approach is based on the Green's function method and Fermi-liquid DFT formalism [80-86]. It generalizes the known Green's function approach by Cederbaum-Domcke (we use this version as a starting basis).

The density of states, which describe the vibrational structure in molecular photoelectron spectra, is calculated with the help of combined DFT-Green's-functions approach. In addition to exact solution of one-bode problem different approaches to calculate reorganization and many-body effects are presented. In all cases no data about the molecular ion are needed and all transitions except those between linear and bent configurations are included. 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 calculation becomes a powerful tool in interpreting the vibrational structure of photoelectron spectra for different molecular systems.

5.2 The combined Green's functions and density functional approach: The Hamiltonian of the system and density of states in one –body solution

According to [65], the quantity which contains the information about the ionization potentials and the molecular vibrational structure due to quick ionization is the density of occupied states[9]:

$$N_k(\epsilon) = (1/2\pi\hbar)\int dt e^{i\hbar^{-1}\epsilon t} \langle \psi_0 | \mathrm{a}^{t}_{k}(0) a_k(t) | \psi_0 \rangle , \tag{5.1}$$

where $|\Psi_0\rangle$ is the exact ground state wavefunction of the reference molecule and $a_k(t)$ is an electron destruction operator, both in the Heisenberg picture. For particle attachment the quantity of interest is the density of unoccupied states:

$$N_k(\epsilon) = (1/2\pi\hbar)\int dt e^{i\hbar^{-1}\epsilon t} \langle \psi_0 | \mathrm{a_k(t)} \mathrm{a}^{t}_{k}(0) | \psi_0 \rangle \tag{5.2}$$

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. The corresponding Hamiltonian is as follows:

$$H = T_{\mathrm{E}}(\partial/\partial x) + T_{\mathrm{N}}(\partial/\partial X) + U(x, X) , \tag{5.3}$$

where T_{E} is the kinetic energy operator for the electrons, T_{N} is the kinetic energy operator for the nuclei, and *U* represents the interaction

$$U(x, X) = U_{\mathrm{EE}}(x) + U_{\mathrm{NN}}(X) + U_{\mathrm{EN}}(x, X) , \tag{5.4}$$

where *x* denotes electron coordinates, *X* denotes nuclear coordinates, U_{EE} represents the Coulomb interaction between electrons, etc.Below we follow to original version of the Cederbaum-Domske approach to vibrational structure of the molecular spectra. Further the following field operator is usually introduced:

$$\Psi(R,\theta,x) = \sum_i \phi_i(x,R,\theta)a_i(R,\theta) \tag{5.5}$$

where the ϕ_i are Hartre-Forck (HF) one–particle functions and the a_i are destruction operators for a HF particle in the state described by the subscript *i*. Fixing $\theta(\theta=\theta_0)$, the Hamiltonian in the occupation number representation is given by [65]

$$H = H_{\mathrm{EN}}(R,\theta_0) + U_{\mathrm{NN}}(R,\theta_0) + T_{\mathrm{N}}(\partial/\partial R), \tag{5.6}$$

$$H_{EN} = \sum_i \epsilon_i(R)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R)a_i^t a_j^t a_l a_k \tag{5.7}$$

$$-\sum_{ij}\sum_{k\in f}[V_{ikkj}(R)]a_i^t a_j, \tag{5.8}$$

$$V_{ijkl} = \langle ij|e^2|r-r'|^{-1}|kl\rangle \tag{5.9}$$

The $\in_i(R)$ are the one-particle HF energies and f denotes the set of orbitals occupied in the HF ground state. As usually in the adiabatic approximation one could write the eigenfunctions to H as products $|x,R,\theta_0\rangle_E \times |R\rangle_N$,and further expand $\in_i(R)$, $V_{ijkl}(R)$, and $U_{NN}(R,\theta)$ about R$_0$ leaving the operators a_i and a_i^t unchanged:

$$H = \sum_i \epsilon_i(R_0)a_i^t a_i + \frac{1}{2}\sum V_{ijkl}(R_0)a_i^t a_j^t a_l a_k -$$
$$-\sum_{ij}\sum_{k\in f}[V_{ikjk}(R_0) - V_{ikkj}(R_0)]a_i^t a_j + + \sum_i \Big[\sum_{s=1}^{M}\left(\frac{\partial \in_1}{\partial R_s}\right)_0 (R-R_{so}) +$$
$$+\frac{1}{2}\sum_i \sum_{s,s'=1}^{M}\left(\frac{\partial^2 \in_i}{\partial R_s \partial R_{s'}}\right)_0 (R_s - R_{so})(R_{s'} - R_{s'0}) \Big] a_i^t a_i + \ldots + U_{NN}(R_0,\theta_0) + \ldots + T_N\left(\frac{\partial}{\partial R}\right) \tag{5.10}$$

where M is the number of normal coordinates.

Choosing R_0 as the equilibrium geometry on the HF level and introducing dimensionless normal coordinates Q_s one can write the following Hamiltonian (the subscript 0 stands for R_0):

$$H = H_E + H_N + H_{EN}^{(1)} + H_{EN}^{(2)} \ , \tag{5.11}$$

$$\begin{aligned} H_E = & \sum_i \epsilon_i(R_0) a_i^t a_i + \frac{1}{2} \sum V_{ijkl}(R_0) a_i^t a_j^t a_l a_k - \\ & - \sum_{i,j} \sum_{k \in f} [V_{ikjk}(R_0) - V_{ikkj}(R_0)] a_i^t a_j \end{aligned} \quad , \tag{5.12}$$

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

$$\begin{aligned} H_{EN}^{(1)} = & \, 2^{-1/2} \sum_{s=1}^{M} \left(\frac{\partial \epsilon_i}{\partial Q_s} \right)_0 (b_s + b_s^t)[a_i^t a_i - n_i] + \\ & + \frac{1}{4} \sum_i \sum_{s,\, s'=1}^{M} \left(\frac{\partial^2 \epsilon_i}{\partial Q_s \partial Q_{s'}} \right)_0 (b_s + b_s^t)(b_{s'} + b_{s'}^t)[a_i^t a_i - n_i], \end{aligned} \tag{5.13}$$

$$\begin{aligned} H_{EN}^{(2)} = & \, 2^{-3/2} \sum \sum_{s=1}^{M} \left(\frac{\partial V_{ijkl}}{\partial Q_s} \right)_0 (b_s + b_s^t)[\delta v_1 a_i^t a_j^t a_k + \\ & + \delta v_2 a_l a_k a_i^t a_j^t + 2 \delta v_3 a_j^t a_k a_l a_i^t] \\ & \frac{1}{8} \sum \sum_{s,s'=1}^{M} \left(\frac{\partial^2 V_{ijkl}}{\partial Q_s \partial Q_{s''}} \right)_0 (b_s + b_s^t)(b_{s'} + \\ & + b_{s'}^t [\delta v_1 a_i^t a_j^t a_k + \delta v_2 a_l a_k a_i^t a_j^t + 2 \delta v_3 a_j^t a_k a_l a_i^t] \end{aligned} \tag{5.14}$$

$$\begin{aligned} n_i &= 1 \qquad i \in f, \qquad & \delta\sigma_f &= 1 \qquad (ijkl) \in \sigma_{f,} \\ &= 0, \qquad i \notin f, & &= 0 \qquad (ijkl) \notin \sigma_f, \end{aligned} \tag{5.15}$$

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.

Besides, here for simplicity all terms leading to anharmonicities are neglected. The ω_s are the HF frequencies and the b_s and b_s^t are destruction and creation operators for vibrational quanta defined by

$$Q_s = (1/\sqrt{2})(b_s + b_s^t), \tag{5.16}$$

$$\partial / \partial Q_s = (1/\sqrt{2})(b_s - b_s^t) \tag{5.17}$$

The interpretation of the above Hamiltonian is given in ref. [3].

The HF-single-particle component H_0 of the Hamiltonian (9) is as follows:

$$\begin{aligned} H_0 = & \sum_i \epsilon_i(R_0) a_i^t a_i + \sum_{s=1}^{M} \hbar\omega_s (b_s^t b_s + \frac{1}{2}) + \\ & + \sum_{s=1}^{M} \sum_i 2^{-1/2} \left(\frac{\partial \epsilon_i}{\partial Q_s} \right) [a_i^t a_i - n_i](b_s + b_s^t)_0 + \\ & + \sum_{s,s'=1} \sum_i \frac{1}{4} \left(\frac{\partial^2 \epsilon_1}{\partial Q_s \partial Q_{s'}} \right)_0 [a_i^t a_i - n_i](b_s + b_s^t)(b_{s'} + b_{s'}^t) \end{aligned} \tag{5.18}$$

Correspondingly in the one-particle picture the density of occupied states is given by [65]

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}\epsilon t} \langle \Phi_0 | \; a_k^t(0) a_k(t) | \; \Phi_0 \rangle, \qquad k \in f \, , \tag{5.19}$$

and the density of unoccupied states by

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\hbar^{-1}\epsilon t} \langle \Phi_0 | \; a_k(t) a_k^t(0) | \; \Phi_0 \rangle, \quad , \quad k \notin f \tag{5.20}$$

with

$$a_k(t) = e^{i\hbar^{-1} H_0 t} a_k e^{-i\hbar^{-1} H_0 t} \, . \tag{5.21}$$

Here $|\Phi_0\rangle$ is the product of the electronic and vibrational ground states, i.e., $|\Phi_0\rangle = |\ \Phi_0\rangle|\ 0\rangle$, where $|\Phi_0\rangle$ is the ground state to the HF operator $\sum \epsilon_i(R_0)a_i^t a_i$ and $|\ 0\rangle$ is the state containing no vibrational quantum, i.e., $b_s|\ 0\rangle = 0$ for all s.

From definitions (5.19) and (5.20) it follows immediately that [65]

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt e^{i\hbar^{-1}(\epsilon-\epsilon_k)t}\langle 0|\ e^{\pm i\hbar^{-1}\tilde{H}_0 t}|0\rangle, \tag{5.22}$$

with

$$\begin{aligned}\tilde{H}_0 = \sum_{s=1}^{M}\ \hbar\omega_s b_s^t b_s + \sum_{s=1}^{M}\ g_s^k(b_s + b_s^t)\\ + \sum_{s,s'=1}^{M}\ \gamma_{ss'}^k(b_s + b_s^t)(b_{s'} + b_{s'}^t)\end{aligned} \tag{5.23}$$

where

$$g_s^i = \pm\frac{1}{\sqrt{2}}\left(\frac{\partial\epsilon_i}{\partial Q_s}\right)_0, \tag{5.24}$$

$$\gamma_{ss'}^i = \pm\frac{1}{4}\left(\frac{\partial^2\epsilon_i}{\partial Q_s\partial Q_{s'}}\right)_0 \tag{5.25}$$

As a first step in the evaluation of Eg. (22) new operators

$$c_s = \sum_{l=1}^{M}\ (\lambda_1^{sl}b_l + \lambda_2^{sl}b_l^t) \tag{5.26}$$

with real coefficients λ_1^{sl}, λ_2^{sl} were introduced in ref. [65]. The coefficients λ_1^{sl}, λ_2^{sl} are now determined in such a way that $\tilde{H}_0$, expressed in the new operators, takes the form

$$\tilde{H}_0 = \sum_{s=1}^{M}\ \hbar\hat{\omega}_s c_s^t c_s + \sum_{s=1}^{M}\ \hat{g}_s(c_s + c_s^t) + k. \tag{5.27}$$

Inserting the inverse transformation

$$b_s = \sum_{l=1}^{M} \lambda_1^{ls} c_l - \lambda_2^{ls} c_l^t) \tag{5.28}$$

in Eg. (23) and comparing with Eg. (28) we obtain the equations

$$\sum_l \hbar\omega_l (\lambda_1^{sl}\lambda_1^{s'l} + \lambda_2^{sl}\lambda_2^{s'l}) + 2\sum_{ll'} \gamma_{ll'}(\lambda_1^{sl} - \lambda_2^{sl})(\lambda_1^{s'l'} - \lambda_2^{s'l'}) = 0 \quad (s \neq s') \tag{5.29}$$

$$\sum_l \hbar\omega_l (\lambda_1^{s'l}\lambda_2^{sl} + \lambda_1^{sl}\lambda_2^{s'l}) - -2\sum_{ll'} \gamma_{ll'}(\lambda_1^{sl} - \lambda_2^{sl})(\lambda_1^{s'l'} - \lambda_2^{s'l'}) = 0 \tag{5.30}$$

$$\hbar\hat{\omega}_s = \sum_l \hbar\omega_l (\lambda_1^{sl} + \lambda_2^{sl})^2 , \tag{5.31}$$

$$\hat{g}_s = \sum_l g_l (\lambda_1^{sl} + \lambda_2^{sl}) \ , \tag{5.32}$$

$$k = \sum_l \frac{1}{2}(\hbar\hat{\omega}_l - \hbar\omega_l) . \tag{5.33}$$

Equation (5.12) and (5.13) together with Eqs. (5.10) and (5.11) constitute a system of $2M^2$ independent equations for the $2M^2$ unknown coefficients λ_1^{sl}, λ_2^{sl}. Solution of this system yields the change in normal coordinates in terms of the coupling constants $\gamma_{ss'}$. Equations (32)-(32) determine the vibrational frequencies $\hat{\omega}_s$ of tion, the new coupling parameters $\hat{g}_s$ and the constant k.

The next unitary operator

$$U = \prod_{l=1}^{M} \exp[f_l (c_l - c_l^t)] \tag{5.34}$$

diagonalizes $\tilde{H}_0$ if

$$f_l = \hat{g}_l / \hbar\hat{\omega} \tag{5.35}$$

is chosen:

$$U\widetilde{H}_0U^t = \sum_s \hbar\hat{\omega}_s c_s^t c_s + \Delta\epsilon \tag{5.36}$$

with

$$\Delta\epsilon = k - \sum_s \hat{g}_s^2 / \hbar\hat{\omega}_s . \tag{5.37}$$

Then the equation (14) can be rewritten as follows [13]:

$$N_k^0(\epsilon) = \frac{1}{2\pi\hbar}\int dt \exp[i\hbar^{-1}(\epsilon - \epsilon_k \pm \Delta\epsilon_k)t]$$
$$\langle 0|\; U^t \exp\left(\pm i\sum_s \hat{\omega}_s c_s^t c_s t\right) U \;|\; 0\rangle \tag{5.38}$$

or using the symbol $|\;\hat{n}\rangle$ for states belonging to operators

$$c_s, \text{i.e.}, c_s^t c_s |\; \hat{n}\rangle = n_s |\; \hat{n}\rangle , \tag{5.39}$$

the density of states takes the form

$$N_k^0(\epsilon) = \sum_{n_1 \cdots n_M} |\; \langle \hat{n}\; | U \;| 0\rangle \;|^2 \delta(\epsilon - \epsilon_k \pm \Delta\epsilon_k \pm n \cdot \hbar\hat{\omega}) \tag{5.40}$$

5.3 The Cederbaum-Domske approach to the many-body problem

Below we give the Cederbaum-Domske perturbation theory approach to *ab initio* calculation of frequencies, geometry shifts, and Franck-Condon factors starting from the one-particle picture discussed above.

In a diagrammatic method in order to obtain the function $N_k(\epsilon)$ one should calculate the Green's function $G_{kk'}(\epsilon)$ first:

$$G_{kk'}(\epsilon) = -i\hbar^{-1}\int_{-\infty}^{\infty} dt e^{i\hbar^{-1}\epsilon t} \langle \psi_0 |\; T\{\; a_k(t)a_k^t(0) \;\} \;|\psi_0\rangle \tag{5.41}$$

where T is Wick's time ordering operator and the function $N_k(\epsilon)$ then follows from relation

$$\pi N_k(\epsilon) = a \operatorname{Im} G_{kk}(\epsilon - ai\eta), \tag{5.42}$$

$a = -sign\epsilon_k$, where η is a positive infinitesimal.

Choosing the unperturbed Hamiltonian H_0 to be

$$H_0 = \sum \epsilon_i a_i^t a_i + H_N \tag{5.43}$$

one finds for the corresponding Green’s functions

$$G_{kk}^0(\epsilon) = \delta_{kk'} / (\epsilon - \epsilon_k - ai\eta) \tag{5.44}$$

The Dyson equation is

$$G_{kk'} = G_{kk'}^0 + \sum_{k''} G_{kk}^0 \Sigma_{kk''} G_{k''k'} \tag{5.45}$$

relates the Green’s functions to the free ones introducing a new function $\Sigma_{kk''}(\epsilon)$ called the (proper) self-energy part.

In in order to calculate $\Sigma_{kk'}$, a well-known diagrammatic method is used. It is useful to remind that the sum of Feynman diagrams leading to the self-energy part is shown in Fig. 1. All notations are standard.

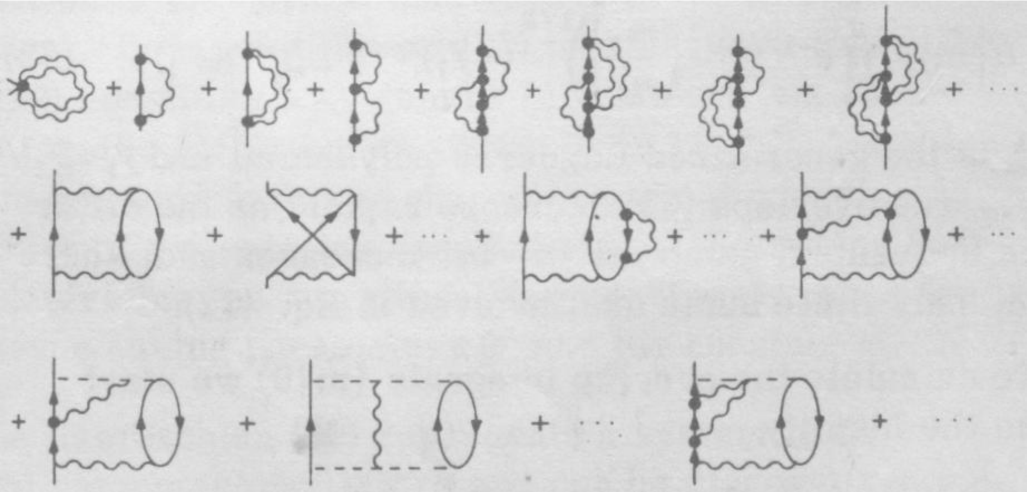

Figure 5.1. The sum of diagrams contributing to the self-energy part

The one-body problem treated above results in the exact solution of the Dyson equation with the self-energy part given by the infinite number of diagrams shown in the first row of Fig. 1 and the corresponding Green's function is as follows [65]:

$$G^{OB}_{kk'}(t) = \pm\delta_{kk'} i \exp\left[-i n^{-1}\left(\varepsilon_k \mp \Delta\varepsilon\right)t\right] \times \sum_n \left|\left\langle \hat{n}_k \middle| U_k \middle| 0\right\rangle\right|^2 \exp\left(\pm i n_k \cdot \hat{\omega}_k t\right) \tag{5.47}$$

The corresponding Dyson-like equation is as follows:

$$G_{kk'}\left(\in\right) = G^{OB}_{kk'}\left(\in\right) + \sum_{kk'} G^{OB}_{kk}\left(\in\right)\hat{O}_{kk''}G_{k''k'}\left(\in\right) \tag{5.48}$$

where $\hat{O}_{kk'}$, is equal to $\Sigma_{kk'}$, less the diagrams of the first row in Fig. 5.1.

The perturbation expansion of Φ is shown in Fig. 2 where $iG^{OB}_{kk'}$, is symbolized by a double solid line.

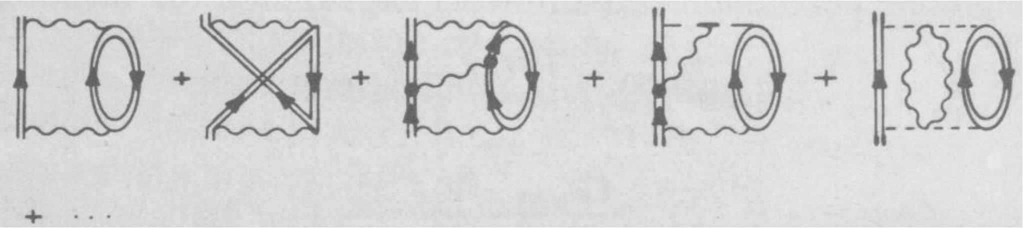

Figure 5.2. Perturbation expansion of Φ_{kk}

The expression for the sum of the first two diagrams appearing in Fig. 5.2 are written by a standard way [65]:

$$
\begin{aligned}
\Phi_{kk'}(\in) = & \sum_{\substack{i,j\in F\\ l\notin F}} \sum_{n_i,n_j,n_l} \frac{\left(V_{klij} - V_{klij}\right)V_{k'lij}U_{n_i i}U_{n_j j}U_{n_l l}}{\in + E_l - E_i - E_j} + \\
& + \sum_{\substack{i,j\in F\\ l\notin F}} \sum_{n_i,n_j,n_l} \frac{\left(V_{klij} - V_{klij}\right)V_{k'lij}U_{n_i i}U_{n_j j}U_{n_l l}}{\in + E_l - E_i - E_j}
\end{aligned}
$$

$$
U_{n_i i=} \left| \langle \hat{n}_i | U_i | 0 \rangle \right|^2 ,
$$

$$
E_i = \in_i \mp \Delta \in_i \mp h\hat{n}_i \cdot \hat{\omega}_i \qquad (5.49)
$$

The direct method for calculation of $N_k(\in)$ as the imaginary part of the corresponding Green's function implicitly includes the determination of the V. I. P. s of the reference molecule and then of $N_k(\in)$. The zeros of the functions

$$
D_k(\in) = \in - \left[\in^{op} + \Sigma(\in)\right]_k , \qquad (5.50)
$$

where $\left(\in^{op} + \Sigma\right)_k$ denotes the *k*th eigenvalue of the diagonal matrix of the one-particle energies added to the matrix of the self-energy part, are the negative V. I. P. 's for a given geometry.

Further it is easily to write:

$$
(V.I.P.)_k = -\left(\in_k + F_k\right), \qquad (5.51)
$$

$$
F_k = \Sigma_{kk}\left(-(V.I.P.)_k\right) \approx \frac{1}{1 - \partial\Sigma_{kk}(\in_k)/\partial_{\in}} \Sigma_{kk}(\in_k). \qquad (5.52)
$$

Expanding the ionic energy E_k^{N-1} 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, [65]*

$$-\left(\frac{\partial(\in_k + F_k)}{\partial Q_s}\right)_0 = \sum_{s' \neq s}\left(\frac{\partial^2(\in_k + F_k)}{\partial Q_s \partial Q_{s'}}\right)_0 \delta Q_{s'}, \tag{5.53}$$

$$+\left[\left(\frac{\partial^2(\in_k + F_k)}{\partial Q_3^2}\right)_0 - h\omega_s\right]\delta Q_s, s = 1 \dots M,$$

where ω_s are frequencies of the reference molecule.

The new coupling constants are then:

$$g_1 = \pm\left(1/\sqrt{2}\right)\left[\partial(\in_k + F_k)/\partial Q_l\right]_0 \tag{5.54}$$

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

Further it can be shown [65-67] that the coupling constants g_l and $y_{ll'}$ are calculated by the well-known perturbation expansion of the self-energy part using the Hamiltonian H_{EN} of Eq. (6). In second order one obtains:

$$\sum_{kk}^{(2)}(\in) = \sum_{\substack{i,j \\ s \notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} + \sum_{\substack{i,j \\ s \notin F}} \frac{(V_{ksij} - V_{ksji})V_{ksij}}{\in + \in_s - \in_i - \in_j} \tag{5.58}$$

and the coupling constant g_l, can be written as

$$g_l \approx \pm\frac{1}{\sqrt{2}}\frac{\partial \in_k}{\partial Q_l}\frac{1 + q_k(\partial/\partial \in)\sum_{kk}\left[-(V.I.P.)_k\right]}{1 - (\partial/\partial \in)\sum_{kk}\left[-(V.I.P.)_k\right]}, \tag{5.59}$$

where

$$q_k = \frac{\sum \frac{(V_{ksij} - V_{ksji})^2}{\left[-(V.I.P.)_k + \in_s - \in_i - \in_j\right]^2}\left[\frac{\partial \in_s}{\partial Q_l} - \frac{\partial \in_i}{\partial Q_l} - \frac{\partial \in_j}{\partial Q_l}\right]}{\frac{\partial \in_k}{\partial Q_l}\sum \frac{(V_{ksij} - V_{ksji})^2}{\left[-(V.I.P.)_k + \in_s - \in_i - \in_j\right]^2}} \tag{5.60}$$

It is suitable to use further the pole strength of the corresponding Green's function

$$\rho_k = \left\{1 - \frac{\partial}{\partial \in} \sum\nolimits_{kk} \left[-(V.I.P.)_k\right]\right\}^{-1} ; 1 \ge \rho_k \ge 0, \tag{5.61}$$

$$g_l \approx g_l^0 \left[\rho_k + q_k(\rho_k - 1)\right], \quad g_l^0 = \pm 2^{-1/2} \partial \in_k / \partial Q_l \tag{5.62}$$

Below we firstly give the DFT definition of the pole strength corresponding to V. I. P.'s and confirm earlier data [65]:

$p_k \approx 0,$8-0,95.

The closeness of p_k to 1 in fact means that a role of the multi-body correlation effects is small ($g_l \approx g_l^0$).

The above presented results can be usefully treated in the terms of the correlation and reorganization effects. Usually it is introduced the following expression for an I.P.:

$$\begin{aligned}(I.P.)_k = -\in_k - \sum_{j \notin, i \in F} \frac{(V_{kikj} - V_{kijk})}{\in_j - \in_i} - \frac{1}{2} \sum_{\substack{i \in F \\ j,l \notin F}} \frac{(V_{kijl} - V_{kilj})}{\in_k + \in_i - \in_j - \in_l} (1 - \delta_{ik}) \\ - \frac{1}{2} \sum_{\substack{p,q \in F \\ j \notin F}} \frac{(V_{kjpq} - V_{kjqp})^2}{\in_k + \in_i - \in_p - \in_q} (1 - \delta_{kp})(1 - \delta_{kq})\end{aligned} \tag{5.64}$$

The first correction term is due to reorganization, the remaining correction terms are due to correlation effects. Then the coupling constant g_l, can be written as

$$g_l \approx g_l^0 \left\{1 + \sum_{j \notin F} \frac{(V_{kkkj})^2}{(\in_j - \in_k)^2} - \frac{1}{2} \left[\begin{aligned} &\sum_{\substack{i \in F \\ j,l \notin F}} \frac{(V_{kijl} - V_{kilj})^2}{(\in_k + \in_i - \in_j - \in_l)^2} (1 - \delta_{ki}) + \\ &+ \sum_{\substack{p,q \in F \\ j, \notin F}} \frac{(V_{kjpq} - V_{kjqp})^2}{(\in_k + \in_i - \in_p - \in_q)^2} (1 - \delta_{kq})(1 - \delta_{kp}) \end{aligned}\right]\right\}$$

(5.65)

The second coupling constant can be written as

$$\gamma_{ll} = \gamma_{ll}^{0}\left(\frac{g_l}{g_l^0}\right) + \frac{1}{4}\sqrt{2}g_l^0 \frac{\partial}{\partial Q_l}\left(\frac{g_l}{g_l^0}\right) \tag{5.66}$$

Notice that γ_{ll}^{0} can be defined analogously to g_l^0.

5.4 Quasiparticle Fermi-liquid density functional theory

In this chapter we present the quasiparticle Fermi-liquid version of the DFT theory, starting from the problem of searching for the optimal one-electron representation and following to refs. [80-87,111]. Two decades ago Davidson had pointed the principal disadvantages of the traditional representation based on the self-consistent field approach and suggested the optimal "natural orbitals" representation [22,23]. Nevertheless there remain insurmountable calculational difficulties in the realization of the Davidson program.

One of the simplified recipes represents, for example, the Kohn-Sham DFT theory [40-42]. In ref. [111] the QED DFT version, based on the formally exact QED perturbation theory (PT), has been developed and a new approach to construction of the optimized one-quasiparticle representation has been proposed. In fact this approach is based on the energy approach, which is well known in the theory of radiative and non-radiative decay of the quasi-stationary states for multielectron systems. The energy approach uses the adiabatic Gell-Mann and Low formula [59] for the energy shift δE with electrodynamic scattering matrices. In a modern theory of molecules there is a number of tasks, where an accurate account for the complex exchange-correlation effects, including the continuum pressure, energy dependence of a mass operator etc., is critically important. It includes also the calculation of the vibration structure for the molecular systems. In this case it can be very useful the quasiparticle DFT [80-87].

In order to get the master equations and construct an optimal basis of the one-particle wave functions φ_λ one could use the Green's function method. Let us define the one-particle Hamiltonian for functions φ_λ so that the Greens' function pole part in the (φ_λ) representation is diagonal on λ. Starting equation is the Dyson equation for multi-electron (for example atom or molecule):

$$(\varepsilon - p^2/2 + \sum Z_\alpha / r_\alpha)\cdot G(x, x', \varepsilon) - \int dx' \sum (x, x', \varepsilon) = \delta(x - x') \quad (5.67)$$

where $x = (r, s)$ are the spatial and spin variables, $\sum$ is the mass operator; Z , as usually, a charge of a nucleus (nuclei) «α», G is the Green's function. In the representation of auxiliary functions φ'_λ the equation (5.67) has the following form:

$$(\varepsilon \cdot \delta_{\lambda\lambda_1} - [\frac{p^2}{2} - \sum \frac{Z_\alpha}{r_\alpha} + \sum (x, x', \varepsilon)]_{\lambda\lambda_1})G_{\lambda\lambda'} = \delta_{\lambda\lambda'} \quad (5.68)$$

where λ_1 is an index of summation. It is natural to choose φ_λ so that the following expression will be diagonal:

$$[p^2/2 - \sum_\alpha Z_\alpha / r_\alpha + \sum (x, x', \varepsilon)]_{\lambda\lambda_1} = E_\lambda(\varepsilon)\cdot \delta_{\lambda\lambda_1} \quad (5.69)$$

Then the Green's function is diagonal on λ:

$$G_{\lambda\lambda'} = G_\lambda \cdot \delta_{\lambda\lambda'}, G_\lambda = 1/[\varepsilon - E_\lambda(\varepsilon)] \quad (5.70)$$

and the functions φ'_λ, which diagonalizes G , satisfy to equation as follows: :

$$\begin{aligned}&(p^2/2 - \sum_\alpha Z_\alpha / r_\alpha)\varphi'_\lambda(x, \varepsilon) + \\ &+ \int \sum (x, x', \varepsilon)\varphi'_\lambda(x_1, \varepsilon)dx_1 - E_\lambda(\varepsilon)\varphi'_\lambda(x, \varepsilon)\end{aligned} \quad (5.71)$$

One could introduce the mixed representation for a mass operator as follows:

$$\sum(x,p,\varepsilon)=\int\sum(x,x_1,\varepsilon)\exp[i(r-r_1)p]dr_1 \qquad (5.72)$$

Then equation (5.71) with account for of the expression (5.72) can be written as follows:

$$\begin{aligned}&[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon)]\varphi_\lambda^/(x,\varepsilon)=\\&=E_\lambda(\varepsilon)\varphi_\lambda^/(x,\varepsilon)\end{aligned} \qquad (5.73)$$

It can be shown that an operator $p=iv$ in (5.67) acts on functions which are on the right of $\sum(x,p,\varepsilon)$. So, in order to find the one-particle energies, defined by the pole part of the Green's function G, it is sufficient to know the functions $\varphi_\lambda^/$ under $\varepsilon=\varepsilon_\lambda$. The Greens' function pole part is as follows:

$$G_{\lambda\lambda^/}=a^\lambda\delta_{\lambda\lambda^/}/(\varepsilon-\varepsilon_\lambda+i\gamma_\lambda) \qquad (5.74)$$

where

$$a^\lambda=1/(1-\partial E_\lambda/\delta\varepsilon)|_{\varepsilon=\varepsilon_\lambda},(\partial E/\partial\varepsilon)|_{\varepsilon=\varepsilon_\lambda}=(\partial E/\partial\varepsilon)|_{\lambda\lambda^/}$$

$$\varepsilon_\lambda=E_\lambda(\varepsilon)=\{p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon)\}|_{\lambda\lambda} \qquad (5.75)$$

The functions $\varphi_\lambda^/(x)=\varphi_\lambda^/(x,\varepsilon_\lambda)$ are satisfying to following equation:

$$[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum(x,p,\varepsilon_\lambda)]\varphi_\lambda=\varepsilon_\lambda\varphi_\lambda(x) \qquad (5.76)$$

Introducing an expansion for self-energy part $\sum$ into set on degrees $x,\varepsilon-\varepsilon_F,p^2-p_F^2$ (here ε_F and p_F are the Fermi energy and pulse correspondingly):

$$\sum(x,p,\varepsilon)=\sum{}_0(x)+(\partial\sum/\partial p^2)(p^2-p_F^2)+$$
$$+(\partial\sum/\partial\varepsilon)(\varepsilon-\varepsilon_F)+...$$

then equation (5.76) is rewritten as follows:

$$[p^2/2-\sum_\alpha Z_\alpha/r_\alpha+\sum{}_0(x)+p(\partial\sum/\partial p^2)p]\Phi_\lambda(x)=$$
$$=(1-\partial\sum/\partial\varepsilon)\varepsilon_\lambda\Phi_\lambda(x) \tag{5.77}$$

The functions Φ_λ in (77) are orthogonal with a weight:

$$\rho_k^{-1}=a^{-1}=[1-\partial\sum/\partial\varepsilon].$$

Now one can introduce the wave functions of the quasiparticles:

$$\varphi_\lambda=a^{-1/2}\Phi_\lambda,$$

which are, as usually, orthogonal with weight 1.

For complete definition of $\{\varphi_\lambda\}$ it should be determined the values $\sum{}_0,\partial\sum/\partial p^2,\partial\sum/\partial\varepsilon$. Naturally, the equations (5.77) can be obtained on the basis of the variational principle, if we start from a Lagrangian of a system L_q (density functional). It should be defined as a functional of the following quasiparticle densities:

$$\nu_0(r)=\sum_\lambda n_\lambda|\Phi_\lambda(r)|^2,$$
$$\nu_1(r)=\sum_\lambda n_\lambda|\nabla\Phi_\lambda(r)|^2, \tag{5.78}$$
$$\nu_2(r)=\sum_\lambda n_\lambda[\Phi_\lambda^*\Phi_\lambda-\Phi_\lambda^*\Phi_\lambda].$$

The densities ν_0 and ν_1 are similar to the HF electron density ρ $(\rho=\nu\cdot a)$ and kinetical energy density correspondingly; the density ν_2 has no an analog in the HFock or standard Kohn-Sham theory and appears as result of account for the energy dependence of the mass operator $\sum$. Lagrangian L_q can be written as sum of a free Lagrangian and Lagrangian of interaction:

$$L_q = L_q^0 + L_q^{\text{int}},$$

where a free Lagrangian L_q^0 has a standard form:

$$L_q^0 = \int dr \sum_{\lambda} n_{\lambda} \Phi_{\lambda}^{*} (i\partial/\partial t - \varepsilon_p)\Phi_{\lambda}, \tag{5.79}$$

And an interaction Lagrangian is defined in the form, which is characteristic for a standard (Kohn-Sham) density functional theory (as a sum of the Coulomb and exchange-correlation terms), however, it takes into account for the energy dependence of a mass operator $\sum$:

$$L_q^{\text{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2} \int \beta_{ik} F(r_1, r_2) \nu_i(r_1) \nu_k(r_2) dr_1 dr_2 \tag{5.80}$$

where β_{ik} are some constants (look below), F is an effective potential of the exchange-correlation interaction. Let us explain here the essence of the introduced constants. Indeed, in some degree they have the same essence as similar constants in well-known Landau Fermi liquid theory and Migdal finite Fermi-systems theory. The Coulomb interaction part L_K looks as follows:

$$\begin{gathered} L_K = -\frac{1}{2}\int [1-\sum{}_2(r_1)]\nu_0(r_1)[1- \\ -\sum{}_2(r_2)]\nu_0(r_2)/|r_1 - r_2| dr_1 dr_2 \end{gathered} \tag{5.81}$$

where $\sum_2 = \partial\sum/\partial\varepsilon$.

Regarding the exchange-correlation potential *F*, it should be noted the there are many possible approximations (directly in the DFT and its modern generalizations). Earlier in our atomic and molecular theories we use the following form:

$$F(r_1,r_2) = X(\int dr\rho_c^{(0)1/3}(r)/|r-r_1||r-r_2| -$$
$$-(\int dr'\rho_c^{(0)1/3}(r')/|r_1-r'| \cdot$$
$$\cdot \int dr''\rho_c^{(0)1/3}(r'')/|r''-r_2|)/<\rho_c^{(0)1/3}>$$
$$<\rho_c^{(0)1/3}> = \int dr\rho_c^{(0)1/3}(r) \qquad (5.82)$$

where X is the numerical coefficient.

It has been obtained in the refs. [80-87] on the basis of calculating the Rayleigh-Schrödinger perturbation theory Feynman diagrams of the second and higher order (so called polarization diagrams) in the Thomas-Fermi approximation. The corresponding relativistic generalization of the potential (5.82) looks as follows [76]:

$$F_{pol}^{d}(r_1r_2) = X(\int dr'\rho_c^{(0)1/3}(r')\theta(r')/|r_1-r'||r'-r_2| -$$
$$-(\int dr'\rho_c^{(0)1/3}(r')\theta(r')/|r_1-r'||\int dr''\rho_c^{(0)1/3}(r'')\theta(r'')/$$
$$/|r''-r_2|)/<\rho_c^{(0)1/3}>);$$

$$<\rho_c^{(0)1/3}> = \int dr\rho_c^{(0)1/3}(r)\theta(r)$$

$$\theta(r) = \{1+[3\pi^2\rho_c^{(0)}(r)]^{2/3}/c^2\}^{1/2}, \qquad (5.83)$$

where c is the light velocity.

Another alternative expression has been introduced by Victor- Laughlin-Taylor (c.f. refs. [24,25]):

$$F(\vec{r}_1,\vec{r}_2) = \frac{1}{r_{12}} - \frac{\alpha_d}{r_1^2 r_2^2}p_1(\cos\theta_{12})w_3(r_2/r_0)w_3(r_2/r_0) -$$
$$-\frac{\alpha_d'}{r_1^3 r_2^3}p_2(\cos\theta_{12})w_4(r_1/r_0)w_4(r_2/r_0) \qquad (5.84)$$

where p_1 are the Legander polynomials, $\cos\theta_{12} = \vec{r}_1\vec{r}_2/(r_1r_2)$.

In the local density approximation in the density functional the potential F can be expressed through the exchange-correlation pseudo-potential V_{XC} as follows [87]:

$$F(r_{1,}r_2) = \delta V_{XC} / \delta v_0 \cdot \delta(r_1 - r_2). \tag{5.85}$$

Further, one can get the following expressions for $\sum_i = -\delta L_q^{\text{int}} / \delta v_1$:

$$\begin{aligned}
&\sum\nolimits_0 = (1 - \sum\nolimits_e) V_K + \sum\nolimits_0^{ex} + \\
&+ \frac{1}{2} \beta_{00} \delta^2 V_{XC} / \delta v^2 \cdot v_0^2 + \beta_{00} \delta V_{XC} / \delta v_0 \cdot v_0 + \\
&+ \beta_{01} \delta V_{XC} / \delta v_0 \cdot v_1 + \beta_{01} \delta^2 V_{XC} / \delta v_0^2 \cdot v_0 v_1 + \\
&+ \beta_{02} \delta^2 V_{XC} / \delta v_0^2 \cdot v_0 v_2 + \beta_{02} \delta V_{XC} / \delta v_0 \cdot v_2
\end{aligned}$$

$$\begin{aligned}
&\sum\nolimits_1 = \beta_{01} \delta V_{XC} / \delta v_0 \cdot v_0 + \beta_{12} \delta V_{XC} / \delta v_0 \cdot v_2 + \\
&+ \beta_{11} \delta V_{XC} / \delta v_0 \cdot v_1;
\end{aligned}$$

$$\begin{aligned}
&\sum\nolimits_2 = \beta_{02} \delta V_{XC} / \delta v_0 \cdot v_0 + \beta_{12} \delta V_{XC} / \delta v_0 \cdot v_1 + \\
&+ \beta_{22} \delta V_{XC} / \delta v_0 \cdot v_2;
\end{aligned} \tag{5.86}$$

Here V_K is the Coulomb term (look above), $\sum_0^{ex}$ is the exchange term. Using the known canonical relationship:

$$H_q = \Phi_\lambda^* \delta L_q / \delta \Phi_\lambda^* + \Phi_\lambda \delta L_q / \delta \Phi_\lambda - L_q$$

after some transformations one can receive the expression for the quasiparticle Hamiltonian, which is corresponding to a Lagrangian L_q:

$$\begin{aligned} &H_q = H_q^0 + H_q^{\mathrm{int}} = H_q^0 - L_K + \\ &+\frac{1}{2}\beta_{00}\delta V_{XC}/\delta v_0 \cdot v_0^2 + \\ &+\beta_{01}\delta V_{XC}/\delta v_0 \cdot v_0 \cdot v_1 + \frac{1}{2}\beta_{11}\delta V_{XC}/\delta v_0 \cdot v_1^2 - \\ &-\frac{1}{2}\beta_{22}\delta V_{XC}/\delta v_0 \cdot v_2^2 \end{aligned} \tag{5.87}$$

Further let us give the corresponding comments regarding the constants β_{ik}.

First of all, it is obvious that the terms with constants $\beta_{01}, \beta_{11}, \beta_{12}, \beta_{22}$ give omitted contribution to the energy functional (at least in the zeroth approximation in comparison with others), so they can be equal to zero. The value for a constant β_{00} in some degree is dependent upon the definition of the potential V_{XC}.

If as V_{XC} it is use one of the correct exchange-correlation potentials from the standard density functional theory, then without losing a community of statement, the constant β_{00} can be equal to 1. The constant β_{02} can be in principle calculated by analytical way, but it is very useful to remember its connection with a spectroscopic factor F_{sp} of atomic or molecular system (it is usually defined from the ionization cross-sections) [60]:

$$F_{sp} = \left\{ 1 - \frac{\partial}{\partial \in} \sum\nolimits_{kk} \left[-(V.I.P.)_k \right] \right\} \tag{5.88}$$

The term $\partial \sum / \partial \varepsilon$ is defined above.

It is easily to understand the this definition is in fact corresponding to the pole strength of the corresponding Green's function [62].

In further calculation as potential V_{XC} we use the exchange-correlation pseudo-potential which contains the correlation (Gunnarsson-Lundqvist) potential and relativistic exchange Kohn-Sham one [40-42]:

$$V_{XC}(r) = f(\theta)V_X(r) - 0{,}0333 \cdot \ln[1 + 18{,}376 \cdot \rho^{1/3}(r)] \tag{5.89}$$

where

$$V_X = -(1/\pi)[3\pi^2 \cdot \rho(r)]^{1/3}$$

is the Kohn-Sham exchange potential, $\theta = [3\pi^2\rho]^{1/3}/c$, and function $f(\theta)$ is as follows:

$$f(\theta) = 3\ln[\theta + (\theta^2+1)^{1/2}]/[2\theta(\theta^2+1)^{1/2}] - 1/2 \qquad (5.90)$$

Using the above written formula, one can simply define values (61), (88). 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.

Further, let us give a short comment regarding an universality of the constants β_{ik}. From the point of view of the analogous universality of the constants in the well-known Landau Fermi-liquid theory and Migdal finite Fermi-systems theory [62]. Indeed, as we know now, the entire universality of the constants in the last theories is absent, though a range of its changing is quite little.

Without a detailed explanation, we note here that the corresponding constants in our theory possess the same universality as ones in the Landau Fermi-liquid theory and Migdal finite Fermi-systems theory. More detailed explanation requires a careful check.

Further it is obvious that omitting the energy dependence of the mass operator (i.e. supposing $\beta_{02} = 0$) the quasiparticle density functional theory can be resulted in the standard Kohn-Sham theory.

Table 5.1.

Spectroscopic factors of the external ns^2 shells of some atoms and ions

Atom, ion	Терм	N	F_{sp}	$F^*_{\exp}\ \tilde{F}_{RPA}$

Ar	1_S	3	0,60	0,56 0,70
TI $^{(IV)}$	1_S	3	0,50	0,34 0,60
Xe	1_S	5	0,36	
TI	2_P	6	0,36	
Pb^+	2_P	6	0,33	
Pb	3_P	6	0,34	
Pb	1_D	6	0,34	
Pb	1_S	6	0,34	
Bi^+	3_P	6	0,32	
Bi	4_S	6	0,33	
Bi	2_D	6	0,33	
Bi	2_P	6	0,33	
Po^+	4_S	6	0,31	
Po	3_P	6	0,31	
Po	1_D	6	0,31	
Po	^1S	6	0,31	
As^+	3_P	6	0,30	
As	2_P	6	0,30	
As^-	1_S	6	0,31	
Rn^+	2_P	6	0,29	

Table 5.1 (continuation).

Spectroscopic factors of the external ns^2 shells of some atoms and ions

Rn	1_S	6	0,29	
Fr^+	1_S	6	0,28	

Fr	2_S	6	0,28	
Ra	1_S	7	0,43	
Ac	2_D	7	0,41	
Ac	2_F	7	0,42	
Th	3_H	7	0,41	
Th	3_F	7	0,42	
Pa	4_I	7	0,42	
U	5_L	7	0,42	

Note: $F^{*}_{\exp}$- experimental value of spectroscopic factor; $\tilde{F}_{RPA}$ is the value, obtained in the random phase approximation with exchange.

In this essence the presented approach to definition of the functions basis $\{\Phi_{\lambda}\}$ of a Hamiltonian H_q can be treated as an improved in comparison with similar basises of other 1-particle representations (HF, Hatree-Fock-Slater, Kohn-Sham etc.). Naturally, this advancement can be manifested during studying those properties of the multi-electron systems, when accurate account for complex exchange-correlation effects, including continuum pressure, energy dependence of mass operator etc., is critically important.

5.5 The application of the combined Green’s function method and quasiparticle DFT approach to diatomics

We choose the diatomic molecules of N_2, CO (and some others) for application of the combined Green’s function method and quasiparticle DFT approach. In ref. [65] it has been shown that the diatomics spectra can be in principle reproduced by applying a one-particle theory with account of the correlation and reorganization effects. The corresponding coupling constants depend on the balance of these effects. The nitrogen molecule has been naturally discussed in many papers. The valence V. I. P. 's of N_2 have been calculated [61,62,65] 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.

In should be reminded that the N_2 molecule is the classical example where the known Koopmans' theorem even fails in reproducing the sequence of the V. I. P. 's in the PE spectrum. From the calculation of Cade *et al.*[71,72] one finds that including reorganization the V. I. P. 's assigned by σ_g and σ_u improve while for the 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. The above-mentioned Green's functions calculation which takes account of reorganization and correlation effects leads to the experimental sequence of V. I. P.'s. In Table 2 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’s functions and DFT approach (e) and corresponding pole strengths (d,e) are listed.

Table 5.2.

The experimental and calculated V. I. P.'s (in eV) of N_2. R_k is the contribution of reorganization; p_k stands for pole strength.

Orbital	Exp VIP a	$-\in_k^b$	$-(\in_k + R_k)^c$	Calc^d V.I.P.'s	ρ_k^d	Calc^e V.I.P.'s	ρ_k^e
$3\sigma_g$	15,6	17,4	16,0	15,5	0,9	15,5	0,9
$1\pi_u$	16,9	17,1	15,7	16,8	0,9	16,8	0,9
$2\sigma_u$	18,8	20,9	19,9	18,6	0,9	18,6	0,8

Therefore, the results, obtained within the Green functions approach and combined method are very much close. Taking into account a simplification of the calculational procedure within the DFT approach, the generalized Cederbaum et al theory looks more attractive else.

As it’s known, of the three bands in the experimental low-energy spectrum of N_2 molecule (Fig. 3), only the $1\pi_u$ band exhibits a strong vibrational structure. When a change of frequency due to ionization is small, the density of states can be well approximated using only one parameter *g:*

$$N_k(\in) = \sum_{n=0}^{\infty} e^{-s} \frac{S^n}{n!} \delta\left(\in - \in_k + \Delta \in_k + n \cdot \hbar\hat{\omega}\right), \qquad (5.70)$$

$$S = g^2 (\hbar\omega)^{-2}$$

In case if the frequencies change considerably, the intensity distribution of the most intensive lines can analogously be well approximated by an effective parameter *S*. In fig.3 the experimental and calculated photoelectron spectra for the N_2 molecule are presented.

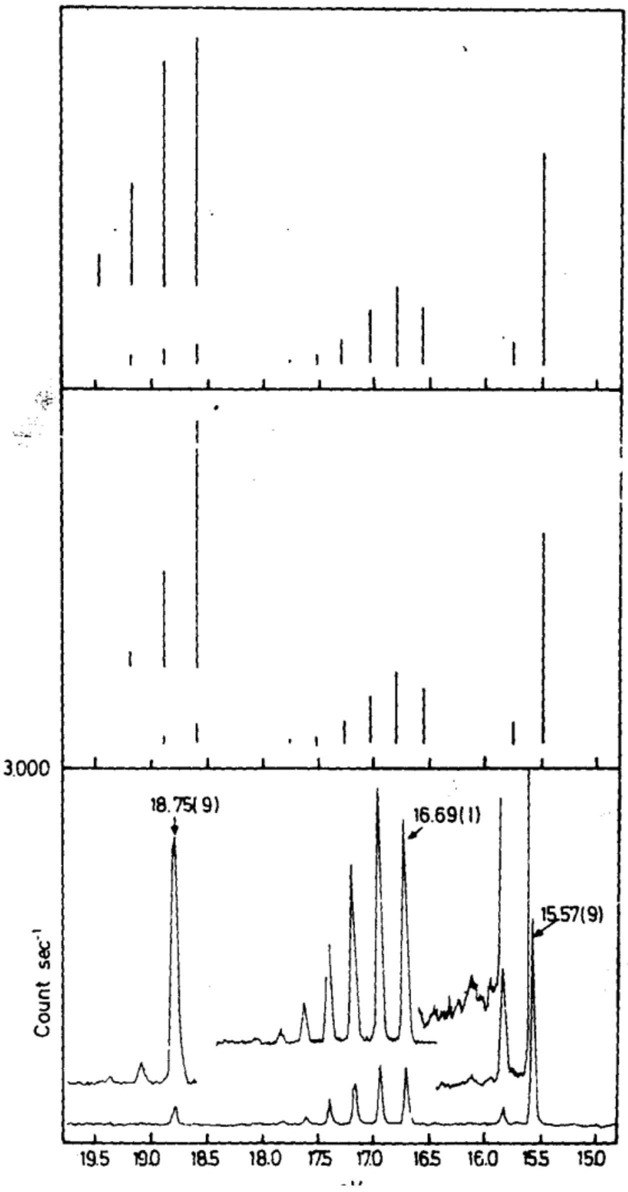

Figure 5.3. Experimental [65]and calculated PE spectra N_2; Uppermost spectrum is calculated with S^0 and Eq. (70). The middle spectrum is calculated with S values from (62) (see text).

The uppermost spectrum is calculated with S^0 (i.e. the constant S calculated with g^0) and Eq. (5.70) [13]. The middle spectrum is calculated with values of S from Eq. (5.62). It is important to note that the original Green's functions and combined Green functions +DFT approach coincide in the scale of the figure. In a whole the agreement between the calculated spectrum (corrected g) and the experimental one is improved. As another example, the molecule CO can be considered.

The experimental and calculated photoelectron spectra for CO molecule are listed in Fig.4. One can see quite physically reasonable agreement between experiment and theory. The original Green's functions [13] and combined Green's functions +DFT approach practically coincide.

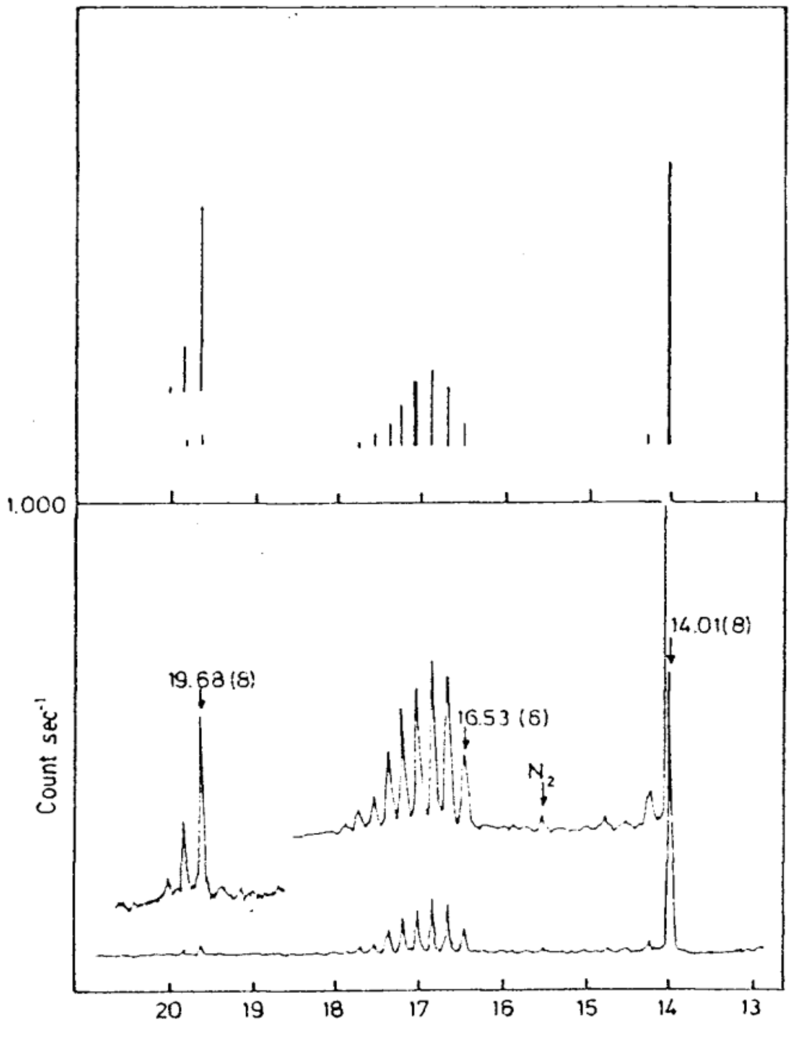

Figure 5.4. The experimental [65] and calculated photoelectron spectra of CO. The upper spectrum is calculated with S^0 and Eq. (70) (see text).

On inclusion of the anharmonicites it should be mentioned that a theory can be generalized by means a standard normal coordinate expansion of Hamiltonian to third and higher orders and correspondingly the theory of the density of states functions N_k developed above can easily be generalized too.

5.6 Summary

In this chapter it has been presented a new combined theoretical approach to vibrational structure in photo-electron spectra of molecules, which is based on the Green's function method and DFT [80-87,111]. In fact approach presented generalizes the standard Green's function approach [65-68]. The density of states, which describe the vibrational structure in molecular photoelectron spectra, is calculated with the help of combined DFT-Green's-functions approach. It is important that the calculational procedure is significantly simplified with using the quasiparticle DFT formalism.

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