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On Numerical Solution of the Integral Hartree–Fock Equations for Molecules by the Method of MO LCAO in the Momentum Space

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To develop a numerical solution of mentioned equations the method of factorized projection of integral operator kernel is applied. All matrix elements of the method are calculated analytically, being expressed in terms of two types of standard integrals: the overlap integrals and one-electron Coulomb integrals. To calculate the integrals we used the O(4)-symmetry of hydrogen-like atomic orbitals as well as operational technique of differentiation with respect to scalar and vector parameters.

Key words: Hartree–Fock equations – MO LCAO – Momentum space – Integral equations.

1. Introduction

In this work we consider the numerical approach to solution of the integral Hartree–Fock equations for molecules. This approach can be used for *ab initio* calculations of terms of many-atomic molecules by the method of MO LCAO. The characteristic property of the approach resides in the fact that the parameters of the AO-exponents are calculated during the solution of Hartree–Fock problem.

This work presents the development and revision of work [1], wherein the approach of factorized projection was presented to solve the integral Hartree–Fock equations for molecules numerically by the method of MO LCAO in momentum space.

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We have chosen the momentum space instead of the coordinate one for two reasons. First, it is possible to rewrite the system of Hartree–Fock equations in the form of a single scalar equation similar to Hartree equation, including, however, exchange part of two-electron interaction. Second, there is an attractive possibility of taking into account the O(4)-symmetry of hydrogen-like AO to transform the integral Hartree–Fock equation to an integral equation describing solely the discrete spectrum of one-electron states. In essence, this transformation implies the conversion to Sturm's eigenvalue problem with the potential, permitting the finite motion only, as in the case of the harmonic oscillator.

This work pursues the practical objective: to develop a suitable algorithm for solution of Hartree–Fock problem for atoms and molecules by the method of MO LCAO; the algorithm, combining analytical rigor with the possibility of analyzing the matrix elements by consideration of separate contributions with clear physical sense.

2. Integral Hartree–Fock Equation for a Closed Electronic Shell of a Molecule and the Method of MO LCAO

Let us write the Hartree–Fock equations for a closed electronic shell of a molecule in the form of a single scalar equation in the momentum space [2]. In the atomic units of length, charge, energy and mass this equation has the form

$$\tfrac{1}{2}(p^2+p_{0i}^2)\psi_i(\boldsymbol{p})-\frac{1}{2\pi^2}\int K(\boldsymbol{p},\boldsymbol{p}')\psi_i(\boldsymbol{p}')\,d^3\boldsymbol{p}'=0. \tag{2.1}$$

The kernel of the integral operator is

$$K(\boldsymbol{p},\boldsymbol{p}')=G(\boldsymbol{p},\boldsymbol{p}')-2F(\boldsymbol{p},\boldsymbol{p}')+f(\boldsymbol{p},\boldsymbol{p}') \tag{2.2}$$

where

$$G(\boldsymbol{p},\boldsymbol{p}')=\sum_a Z_a \exp\left[-i(\boldsymbol{p}-\boldsymbol{p}')\boldsymbol{R}_a\right](\boldsymbol{p}-\boldsymbol{p}')^{-2}, \tag{2.3a}$$

$$F(\boldsymbol{p},\boldsymbol{p}')=\sum_{j=1}^{n_e/2}\int \psi_j^*(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\,d^3\boldsymbol{\eta}(\boldsymbol{p}-\boldsymbol{p}')^{-2}, \tag{2.3b}$$

$$f(\boldsymbol{p},\boldsymbol{p}')=\sum_{j=1}^{n_e/2}\int \eta^{-2}\psi_j^*(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\,d^3\boldsymbol{\eta}, \tag{2.3c}$$

Z_a and $\boldsymbol{R}_a$ are the charge and the coordinates of ath nucleus in the molecule respectively.

It is easy to check, that the kernel $K(\boldsymbol{p},\boldsymbol{p}')$ has the Hermitian character:

$$K(\boldsymbol{p},\boldsymbol{p}')=K^*(\boldsymbol{p}',\boldsymbol{p})$$

where the sign * means the complex conjugation. The parameter p_{0i} is connected with the energy ε_i of the ith electron by the relation

$$p_{0i}^2=-2\varepsilon_i. \tag{2.4}$$

When the spectrum is discrete, the parameter p_{0i} is a real number, when the spectrum is continuous, p_{0i} becomes an imaginary number.

The integral Eq. (2.1) is an integral equation of the third kind.

The Eq. (2.1) can be reduced to an integral equation of the second kind by means of transformation of momentum $\boldsymbol{p}$ from Cartesian coordinates to Fock coordinates [3]. The latter determine the surface of 4-dimensional unit sphere in terms of the angles α, θ, φ.

Fock transformation for the momentum p has the form

$$\begin{aligned}
\xi &= \frac{2p_{0i}p_x}{p_{0i}^2+p^2} = \sin\alpha\,\sin\theta\,\cos\varphi,\\
\eta &= \frac{2p_{0i}p_y}{p_{0i}^2+p^2} = \sin\alpha\,\sin\theta\,\sin\varphi,\\
\zeta &= \frac{2p_{0i}p_z}{p_{0i}^2+p^2} = \sin\alpha\,\cos\theta,\\
\chi &= \frac{p_{0i}^2-p^2}{p_{0i}^2+p^2} = \cos\alpha, \qquad \alpha,\theta\in[0,\pi], \quad \varphi\in[0,2\pi].
\end{aligned} \tag{2.5}$$

The wave-function of ith electron can be transformed with the help of Eq. (2.5) as follows:

$$\psi_i(\boldsymbol{p}) = 2^{3/2}\pi^{-1}p_{0i}^{5/2}(p_{0i}^2+p^2)^{-2}\Psi_i(\alpha,\theta,\varphi). \tag{2.6}$$

The function $\Psi_i(\alpha,\theta,\varphi)$ satisfies the integral equation of the second kind

$$p_{0i}\Psi_i(\Omega_i) = (2\pi^2)^{-1}\int K(\Omega_i,\Omega_i')\Psi_i(\Omega_i')\,d\Omega_i', \tag{2.7}$$

where

$$K(\Omega_i,\Omega_i') = G(\Omega_i,\Omega_i') - 2F(\Omega_i,\Omega_i') + f(\Omega_i,\Omega_i') \qquad i=1,2,\ldots,n_e/2, \tag{2.8}$$

and

$$G(\Omega_i,\Omega_i') = \sum_a Z_a\, e^{-i(\boldsymbol{p}-\boldsymbol{p}')\boldsymbol{R}_a}[4\sin^2(\omega_i/2)]^{-1}, \tag{2.9a}$$

$$F(\Omega_i,\Omega_i') = \sum_{j=1}^{n_e/2}\int \psi_j^*(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\,d^3\boldsymbol{\eta}[4\sin^2(\omega_i/2)]^{-1}, \tag{2.9b}$$

$$f(\Omega_i,\Omega_i') = \sum_{j=1}^{n_e/2}\int \eta^{-2}\psi_j^*(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\,d^3\boldsymbol{\eta}(p^2+p_{0i}^2)(p'^2+p_{0i}^2). \tag{2.9c}$$

The symbol Ω_i stands for the set of angles $(\alpha_i,\theta_i,\varphi_i)$, the surface element of 4-sphere $d\Omega_i = \sin^2\alpha_i\cdot\sin\theta_i\,d\alpha_i\,d\theta_i\,d\varphi_i$, ω_i means the angle between the points of 4-sphere, which have the coordinates Ω_i and Ω_i'.

To solve the integral equation (2.7) means to find the expansion of the kernel $K(\Omega_i,\Omega_i')$ in bilinear series of functions, which depend on arguments Ω_i and Ω_i'

separately. The calculation of these functions provides the solution of eigenvalue problem (2.7).

In case of a single electron we have $F = f = 0$. Then, as was shown in [4], the expansion of $[4 \sin^2 (\omega_i/2)]^{-1}$ in series of 4-dimensional spherical harmonics with subsequent diagonalization of the overlap matrix of the harmonics, centered in atoms of the molecule, yields exact solution of one-electron Schrödinger equation in the form of MO LCAO. The same form of the solution was obtained in [5].

Comparing the kernels G and F in Eq. (2.9) and taking into account the normalization property of the functions $\psi_j(\boldsymbol{p})$ we can make a conclusion that the singular part, $[4 \sin^2 (\omega_i/2)]^{-1}$, of the kernel K determines (in case of molecules with non-negative total charge) the character of discrete electronic terms, their denumerable set having a point of level, crowding similar to one of a hydrogen-like atom.

The exchange part f (2.9c) of the kernel K does not have singularities at $\boldsymbol{p} = \boldsymbol{p}'$, while the function $F(\boldsymbol{p}, \boldsymbol{p}')$ is finite when $p \to \infty$ and/or $p' \to \infty$ as a consequence of relation (2.6).

However, in case of negatively charged molecules the exchange part of interaction f can play a leading role in determination of the character of the set of electronic terms by stabilization of the interaction between nuclei and electrons of the molecule in the Hartree–Fock equation, the denumerable set of terms becoming finite or empty. The emptiness of the set means that the Hartree–Fock equation (2.7) is not applicable for the description of a given stable molecular system. In this case the consideration of correlation between the motion of electrons in the molecule is of principal importance.

When solving the Eq. (2.7), one usually encounters two questions. The first is how to find initial models of MO $\psi_i(\boldsymbol{p})$ for the purpose of calculation of kernels F and f. The second is how to construct the bilinear expansion of the kernel K (2.8) of the integral equation (2.7) for these initial models. These questions are interrelated.

From the viewpoint of numerical solution of Eq. (2.7) the account of asymptotic properties of MO ψ_j at $p \to \infty$ does not seem to be important. However, a consideration of these properties seems essential to us, since the similarity of the MO-asymptotic forms for Schrödinger equation with the kernel (2.9a) and for Hartree–Fock equation with the kernel (2.8) shows the expediency to apply the hydrogen-like AO for bilinear expansion of the kernel K as well as for modelling the initial MO when calculating the kernels F and f. Schrödinger's MO have the following valuable feature. Being substituted into the integrals (2.9b) and (2.9c) they do not result in the appearance of the functions with asymptotic forms other than AO of hydrogen-like type (HAO) in the expansions of the kernels F and f. This feature of HAO is of principal importance both in the theory of Hartree–Fock equation (2.7), and in the development of numerical approaches to its solution. Therefore, we suppose, that the basis of HAO is the most natural for numerical solution of the Eq. (2.7).

To solve the integral equation (2.7) numerically let us apply the method of factorized projection of the kernel (2.8) developed in [1]. Formally speaking, the method consists in the solution of the system of equations

$$\sum_n [\lambda (u_m, u_n)\boldsymbol{c}_n - (u_m, Ku_n)\boldsymbol{c}_n] = 0 \tag{2.10}$$

where u_n are the basis functions, K is the kernel (2.8), λ is a parameter of the equation, $\boldsymbol{c}_n$ is an eigenvector of the equation, (u_m, u_n) and (u_m, Ku_n) are the matrix elements.

Since the kernel K algebraically depends on the eigenvectors $\boldsymbol{c}_n$, the Eqs. (2.10) are algebraic. When the kernel K is fixed with respect to $\boldsymbol{c}_n$, these equations become linear. Therefore, at each iteration the problem is reduced to combined diagonalization of two Hermitian matrices of finite dimension, the main problem consisting in the calculation of the matrix elements of (u_m, u_n) and (u_m, Ku_n).

3. Derivation of Expressions for the Matrix Elements

So, we take 4-dimensional spherical harmonics $\Psi_{nlm}(\Omega_i)\, e^{i\boldsymbol{p}\boldsymbol{R}_k}$, centered in the nuclei of the molecule, as the basis functions, which the solution $\Psi_i(\Omega_i)$ is projected on. The integer numbers n, l and m define a spherical harmonic on the surface of 4-dimensional sphere, the index k being equal to the number of a nucleus with coordinates $\boldsymbol{R}_k$.

The matrix equation for eigenvectors $\boldsymbol{c}_i$ and eigenvalues p_{0i} has the form

$$p_{0i}\boldsymbol{S}\boldsymbol{c}_i = \boldsymbol{H}\boldsymbol{c}_i \tag{3.1}$$

where the matrix elements are defined by the following integrals

$$S_{nlmk}^{n'l'm'k'} = \frac{1}{2\pi^2} \int e^{i\boldsymbol{p}\boldsymbol{R}_{kk'}} \Psi_{nlm}(\Omega_i) \Psi^*_{n'l'm'}(\Omega_i)\, d\Omega_i,$$
$$\boldsymbol{R}_{kk'} = \boldsymbol{R}_k - \boldsymbol{R}_{k'}, \tag{3.2}$$

$$H_{nlmk}^{n'l'm'k'} = \frac{1}{2\pi^2} \int\int e^{i\boldsymbol{p}\boldsymbol{R}_k} \Psi_{nlm}(\Omega_i) K(\Omega_i, \Omega_i')$$
$$\times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'}} \Psi^*_{n'l'm'}(\Omega_i')\, d\Omega_i'\, d\Omega_i. \tag{3.3}$$

The matrix elements of S-type represent the overlap integrals of the basis functions centered in the nuclei of the molecule.

The matrix elements of H-type include one-electron integrals of the interaction between electrons and nuclei of the molecule as well as interaction integrals of the electrons.

Consider the calculation of all these integrals in succession.

3.1. *Matrix Elements of S*

The matrix elements $S_{nlmk}^{n'l'm'k'}$ of (3.2) were calculated in [6], where they were designated as $S_{nlm}^{n'l'm'}(\boldsymbol{R}_{kk'})$. The matrix elements of S can be calculated with the help of Wigner–Biedenharn theorem [7] about the expansion of a product of O(4)-harmonics in finite series of O(4)-harmonics with subsequent application of Fourier-transformation of HAO from momentum space to coordinate space.

The final result for the matrix element of S is as follows:

$$S_{nlmk}^{n'l'm'k'} = \sum_{NLM} \pi^{1/2} p_{0i}^{-3/2} u_{Np_{0i},NLM}(\boldsymbol{R}_{kk'}) T(nlm, n'l'm'; NLM), \tag{3.4}$$

where $u_{Np_{0i};NLM}(\boldsymbol{R})$ is HAO in the coordinate space, and

$$T(nlm, n'l'm'; NLM) = (2\pi^2)^{-1} \int \frac{4p_{0i}^2}{p_{0i}^2 + p^2} \Psi^*_{n'l'm'}(\Omega_i) \times \Psi_{nlm}(\Omega_i) \Psi^*_{NLM}(\Omega_i)\, d\Omega_i. \tag{3.5}$$

The coefficients T are calculated in terms of the integrals of the product of three O(4)-harmonics in a following way:

$$T(nlm, n'l'm'; NLM) = 2C(nlm, n'l'm'; NLM) + \sum_{\nu=|N-2|+1(2)N+1} C^*(n'l'm', \nu LM; nlm) \times C^*(NLM, 200; \nu LM), \tag{3.6}$$

where

$$C(nlm, n'l'm'; NLM) = \frac{1}{2\pi^2} \int \Psi_{nlm}(\Omega_i) \Psi_{n'l'm'}(\Omega_i) \times \Psi^*_{NLM}(\Omega_i)\, d\Omega_i. \tag{3.7}$$

In a special article we shall consider the practical calculation of the coefficients $C(nlm, n'l'm', NLM)$. Here we note that the coefficients (3.7) become zero unless the numbers N, L, M satisfy the following conditions

$$\begin{aligned} &N = |n-n'|+1, |n-n'|+3, \ldots, n+n'-3, n+n'-1, \\ &N > L = |l-l'|, |l-l'|+2, \ldots, l+l'-2, l+l', \\ &M = m+m'. \end{aligned} \tag{3.7a}$$

Hydrogen-like atomic orbitals have the following form in the coordinate space

$$u_{Np_{0i},NLM}(\boldsymbol{r}) = R_{NL}(p_{0i}r)\, Y_{LM}(\hat{\boldsymbol{r}}), \tag{3.8}$$

where

$$R_{NL}(p_{0i}r) = C_{NL}(2p_{0i}r)^L L_{N-L-1}^{2L+1}(2p_{0i}r)\, e^{-p_{0i}r} \tag{3.9}$$

$Y_{lm}(\hat{\boldsymbol{r}})$ is the spherical function in R_3, $L_n^{\alpha}(z)$ is the associated Laguerre polynomial [8],

$$C_{NL} = 2p_{0i}^{3/2}[N(N+L)!/(N-L-1)!^{-1/2}, \tag{3.10}$$

$\hat{\boldsymbol{r}}$ is a unit vector in the direction of $\boldsymbol{r}$.

3.2. *Matrix elements of* H

To calculate the matrix elements of H-type (3.3) it is necessary to have the approximations for molecular orbitals with which the kernels F and f can be calculated.

In the method of factorized projection of the kernel (2.8) the wave functions ψ_i are constructed in the form of LCAO or their iterations by the kernel (2.8) of the integral equation (2.7). That is why our calculations of the matrix elements of H may have various degrees of complication depending on the chosen way of construction of ψ_i. Let us choose the method of construction of $\psi_i(\boldsymbol{p})$ in the form of LCAO with AO having HAO-type given in the momentum space as follows:

$$\psi_i(\boldsymbol{p}) = \sum_{NLMa} c_{NLMa}^{i} e^{-i\boldsymbol{p}\boldsymbol{R}_a} \psi_{i,NLM}^{*}(\boldsymbol{p}) \tag{3.11}$$

where HAO $\psi_{i,NLM}^{*}(\boldsymbol{p})$ has the form

$$\psi_{i,NLM}^{*}(\boldsymbol{p}) = 2^{3/2}\pi^{-1}p_{0i}^{5/2}(p_{0i}^2+p^2)^{-2}\Psi_{i,NLM}^{*}(p,\theta,\varphi), \tag{3.12}$$

where

$$\Psi_{i,NLM}(p,\theta,\varphi) = b_{NL}\left(\frac{2p_{0i}p}{p_{0i}^2+p^2}\right)^{L} C_{N-L-1}^{L+1}\left(\frac{p_{0i}^2-p^2}{p_{0i}^2+p^2}\right)\bar{Y}_{LM}(\theta,\varphi), \tag{3.13}$$

$C_n^{\alpha}(z)$ is the Gegenbauer polynomial [8], $b_{NL} = (-1)^{N+L+1}\cdot 2\pi^{1/2}[N(N-L-1)!/(N+L)!]^{1/2}$, $\bar{Y}_{LM}(\theta,\varphi)$ is the modified spherical harmonic which is related to the usual spherical harmonic:

$$\bar{Y}_{LM}(\theta,\varphi) = (-i)^{L}Y_{LM}(\theta,\varphi). \tag{3.14}$$

With the help of the coordinates (2.5) the function $\Psi_{NLM}(p,\theta,\varphi)$ can be rewritten as a 4-dimensional spherical harmonic, which depends on the angles α, θ and φ:

$$\Psi_{NLM}(\alpha,\theta,\varphi) = b_{NL}\sin^{L}\alpha C_{N-L-1}^{L+1}(\cos\alpha)\bar{Y}_{LM}(\theta,\varphi). \tag{3.15}$$

Now let us calculate the kernels $F(\Omega_i,\Omega_i')$ and $f(\Omega_i,\Omega_i')$ given by the formulae (2.9b, c).

$$F = \sum_{j=1}^{n_e/2} F_j[4\sin^2(\omega_i/2)]^{-1} \tag{3.16}$$

where

$$F_j = \int \psi_j^{*}(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\,d^3\boldsymbol{\eta}. \tag{3.17}$$

$$f = \sum_{j=1}^{n_e/2} f_j(p^2+p_{0i}^2)(p'^2+p_{0i}^2) \tag{3.18}$$

where

$$f_j = \int \eta^{-2}\psi_j^*(\boldsymbol{p}'-\boldsymbol{\eta})\psi_j(\boldsymbol{p}-\boldsymbol{\eta})\, d^3\boldsymbol{\eta}. \tag{3.19}$$

Let us substitute the function $\psi_j(\boldsymbol{p})$ which is given by the expression (3.11) into the integrals F_j and f_j.

$$F_j = \sum_{NLMa} \sum_{N'L'M'a'} c^*_{j,NLMa} c_{j,N'L'M'a'} \times e^{i\boldsymbol{p}'\boldsymbol{R}_{a'}-i\boldsymbol{p}\boldsymbol{R}_a} \int e^{i\boldsymbol{\eta}\boldsymbol{R}_{aa'}}\psi_{j,N'L'M'}(\boldsymbol{p}'-\boldsymbol{\eta})\psi^*_{j,NLM}(\boldsymbol{p}-\boldsymbol{\eta})\, d^3\boldsymbol{\eta} \tag{3.20}$$

$$f_j = \sum_{NLMa} \sum_{N'L'M'a'} c^*_{j,NLMa} c_{j,N'L'M'a'} \times e^{i\boldsymbol{p}'\boldsymbol{R}_{a'}-i\boldsymbol{p}\boldsymbol{R}_a} \int e^{i\boldsymbol{\eta}\boldsymbol{R}_{aa'}}\eta^{-2}\psi_{j,N'L'M'}(\boldsymbol{p}'-\boldsymbol{\eta})\psi^*_{j,NLM}(\boldsymbol{p}-\boldsymbol{\eta})\, d^3\boldsymbol{\eta}. \tag{3.21}$$

The calculation of the integrals over $d^3\boldsymbol{\eta}$ in Eqs. (3.20) and (3.21) presents a serious problem.

The substitution of Eqs. (3.20) and (3.21) into Eqs. (3.16) and (3.18) respectively, followed by the substitution of the kernels F and f into the matrix element of H (3.3) yields the following general expression:

$$\begin{aligned}
H^{n'l'm'k'}_{nlmk} = \frac{1}{2\pi^2}\Bigg[& \sum_a Z_a \iint e^{i\boldsymbol{p}\boldsymbol{R}_{ka}}\Psi_{nlm}(\Omega_i) \\
& \times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a}}\Psi^*_{n'l'm'}(\Omega_i')\left[4\sin^2\frac{\omega_i}{2}\right]^{-1} d\Omega_i\, d\Omega_i' \\
& - 2\sum_{j=1}^{n_e/2} \sum_{NLMa} \sum_{N'L'M'a'} c^*_{j,NLMa} c_{j,N'L'M'a'} \iint e^{i\boldsymbol{p}\boldsymbol{R}_{ka}}\Psi_{nlm}(\Omega_i) \\
& \times \int e^{i\boldsymbol{\eta}\boldsymbol{R}_{aa'}}\psi_{j,N'L'M'}(\boldsymbol{p}'-\boldsymbol{\eta})\psi^*_{j,NLM}(\boldsymbol{p}-\boldsymbol{\eta})\, d^3\boldsymbol{\eta} \\
& \times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}}\Psi^*_{n'l'm'}(\Omega_i')[4\sin^2(\omega_i/2)]^{-1}\, d\Omega_i\, d\Omega_i' \\
& + \sum_{j=1}^{n_e/2} \sum_{NLMa} \sum_{N'L'M'a'} c^*_{j,NLMa} c_{j,N'L'M'a'} \\
& \times \iint e^{i\boldsymbol{p}\boldsymbol{R}_{ka}}\Psi_{nlm}(\Omega_i)(p^2+p_{0i}^2) \\
& \times \int e^{i\boldsymbol{\eta}\boldsymbol{R}_{aa'}}\eta^{-2}\psi_{j,N'L'M'}(\boldsymbol{p}'-\boldsymbol{\eta})\psi^*_{j,NLM}(\boldsymbol{p}-\boldsymbol{\eta})\, d^3\boldsymbol{\eta} \\
& \times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}}\Psi^*_{n'l'm'}(\Omega_i')(p'^2+p_{0i}^2)\, d\Omega_i\, d\Omega_i'\Bigg].
\end{aligned} \tag{3.22}$$

Investigation of Eq. (3.22) shows that the calculations of all the integrals require an addition theorem for HAO in the momentum space. Such a theorem cannot be obtained in terms of a finite sum, therefore we need such a formulation of the theorem that the series factorizing the function $\psi_{nlm}(\boldsymbol{p}-\boldsymbol{\eta})$ with respect to the arguments $\boldsymbol{p}$ and $\boldsymbol{\eta}$, should have minimal number of indices of the infinite summation.

We derived such a theorem in [9]. In this work we present the expression omitting the derivation:

$$\psi_{p_{01},nlm}(\boldsymbol{p}-\boldsymbol{k}) = 4(\pi p_{02})^{1/2} \sum_{NLM} (-1)^L (p_{02}^2 + p^2)^{-1} \Psi_{p_{02},NLM}(\boldsymbol{p}) \times \sum_{N'L'M'} G_{LM;lm}^{L'M'} B_{nl;NL}^{N'L'} \psi_{p_0,N'L'M'}(\boldsymbol{k}) \tag{3.23}$$

where $p_0 = p_{01} + p_{02}$. The sum is finite with respect to the indices $N'L'M'$, L, M, being infinite with respect to N.

In the Eq. (3.23) the coefficient $G_{LM;lm}^{L'M'}$ is well-known Gaunt integral,

$$G_{LM;lm}^{L'M'} = \int_0^{\pi} \int_0^{2\pi} Y_{lm}(\theta, \varphi) Y_{LM}(\theta, \varphi) Y_{L'M'}^*(\theta, \varphi) \sin\theta \, d\theta \, d\varphi, \tag{3.24}$$

the coefficient $B_{nl;NL}^{N'L'}$ is determined by the expression

$$B_{nl;NL}^{N'L'} = C_{nl} C_{NL} C_{N'L'}^{-1} [\Gamma(N'+L'+1)]^{-1} \times \sum_{\alpha=0}^{n-l-1} \sum_{\beta=0}^{N-L-1} (-1)^{\alpha+\beta} (L'-l-L-\alpha-\beta)_{N'-L'-1} (\alpha!\beta!)^{-1} \times (p_{01}/p_0)^{\alpha} (p_{02}/p_0)^{\beta} \Gamma(L'+l+L+2+\alpha+\beta) \times \binom{n+l}{n-l-1-\alpha} \binom{N+L}{N-L-1-\beta}, \tag{3.25}$$

the coefficients $C_{N'L'}$ being given by Eq. (3.10), wherein p_{0i} should be substituted by the parameter p_0.

As we see from the expansion (3.23), HAO $\Psi_{p_{02},NLM}(\boldsymbol{p})$ and $\psi_{p_0,N'L'M'}(\boldsymbol{k})$ belong to spaces with different scales characterized by the parameters p_{02} and p_0 respectively. The parameter p_{02} is arbitrary in the region of positive real numbers and it is to be chosen as applied to a concrete problem.

Let us consider the expression (3.22) which is the sum of three contributions: one-electron contribution as well as Coulomb and exchange two-electron contributions.

By means of addition theorem (3.23) for HAO $\psi_{i,NLM}(\boldsymbol{p}-\boldsymbol{\eta})$ and $\psi_{i,N'L'M'}(\boldsymbol{p}'-\boldsymbol{\eta})$ we can reduce two-electron integrals to overlap integrals of HAO and one-electron integrals occurring in the first contribution to Eq. (3.22). In this connection a curious fact should be mentioned that two-electron exchange integrals are calculated more easily than Coulomb integrals, since the former include two infinite summations, while the latter include one more infinite summation arising

when calculating the Coulomb integrals of one-electron type. Note that two-electron Coulomb integrals can also be reduced to double infinite summation. In this case, however, one-electron Coulomb integrals arise which are more complicated than the standard integrals we want to reduce the problem of calculating the matrix element (3.22) to.

Although our misgivings of that kind may not be well-founded, we prefer the way of calculation described in what follows.

So we first calculate the integrals over $d^3\boldsymbol{\eta}$ in Eq. (3.22), i.e. the quantities constituting F_j and f_j.

Let us introduce the notation:

$$F_j(NLM, N'L'M', \boldsymbol{R}) = \int e^{i\boldsymbol{\eta}\boldsymbol{R}} \psi_{j,N'L'M'}(\boldsymbol{p}' - \boldsymbol{\eta}) \psi^*_{j,NLM}(\boldsymbol{p} - \boldsymbol{\eta})\, d^3\boldsymbol{\eta}, \tag{3.26}$$

$$f_j(NLM, N'L'M', \boldsymbol{R}) = \int e^{i\boldsymbol{\eta}\boldsymbol{R}} \eta^{-2} \psi_{j,N'L'M'}(\boldsymbol{p}' - \boldsymbol{\eta}) \psi^*_{j,NLM}(\boldsymbol{p} - \boldsymbol{\eta})\, d^3\boldsymbol{\eta}. \tag{3.27}$$

Substituting the expansion (3.23), where we put $p_{01} = p_{0j}$, $p_{02} = p_{0i}$ into Eqs. (3.26) and (3.27), then we have

$$\begin{aligned} F_j(NLM, N'L'M', \boldsymbol{R}) = 16\pi p_{0i} \sum_{N_1'L_1'M_1'} (-1)^{L_1+L_1'} (p_{0i}^2 + p^2)^{-1} (p_{0i}^2 + p'^2)^{-1} \\ \times \Psi^*_{p_{0i},N_1L_1M_1}(\boldsymbol{p}) \Psi_{p_{0i},N_1'L_1'M_1'}(\boldsymbol{p}') \\ \times \sum_{N_2L_2M_2} \sum_{N_2'L_2'M_2'} G^{L_2M_2}_{L_1M_1;LM} B^{N_2L_2}_{NL;N_1L_1} \\ \times G^{L_2'M_2'}_{L_1'M_1';L'M'} B^{N_2'L_2'}_{N'L';N_1'L_1'} \\ \times \int \psi^*_{p_0,N_2L_2M_2}(\boldsymbol{\eta}) \psi_{p_0,N_2'L_2'M_2'}(\boldsymbol{\eta})\, e^{i\boldsymbol{\eta}\boldsymbol{R}}\, d^3\boldsymbol{\eta}; \end{aligned} \tag{3.28}$$

$$\begin{aligned} f_j(NLM, N'L'M', \boldsymbol{R}) = 16\pi p_{0i} \sum_{N_1L_1M_1} \sum_{N_1'L_1'M_1'} (-1)^{L_1+L_1'} (p_{0i}^2 + p^2)^{-1} (p_{0i}^2 + p'^2)^{-1} \\ \times \Psi^*_{p_{0i},N_1L_1M_1}(\boldsymbol{p}) \Psi_{p_{0i},N_1'L_1'M_1'}(\boldsymbol{p}') \\ \times \sum_{N_2L_2M_2} \sum_{N_2'L_2'M_2'} G^{L_2M_2}_{L_1M_1;LM} B^{N_2L_2}_{NL;N_1L_1} \\ \times G^{L_2'M_2'}_{L_1'M_1';L'M'} B^{N_2'L_2'}_{N'L';N_1'L_1'} \\ \times \int e^{i\boldsymbol{\eta}\boldsymbol{R}} \eta^{-2} \psi^*_{p_0,N_2L_2M_2}(\boldsymbol{\eta}) \psi_{p_0,N_2'L_2'M_2'}(\boldsymbol{\eta})\, d^3\boldsymbol{\eta}, \end{aligned} \tag{3.29}$$

where $p_0 = p_{0i} + p_{0j}$. The integrals over $d^3\boldsymbol{\eta}$ in Eqs. (3.28) and (3.29) can be calculated in a closed form. This will be done later.

Let us substitute the expressions (3.28) and (3.29) into the matrix element (3.22). After some algebra we obtain the following integrals over the variables Ω_i and Ω_i':

(1) The integrals of one-electron part

$$Q_1 = \int\int e^{i\boldsymbol{p}\boldsymbol{R}_{ka}} \Psi_{nlm}(\Omega_i)[4\sin^2(\omega_i/2)]^{-1} \times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}} \Psi^*_{n'l'm'}(\Omega'_i)\, d\Omega_i\, d\Omega'_i. \tag{3.30}$$

(2) The integrals of two-electron Coulomb part

$$Q_2 = \int\int e^{i\boldsymbol{p}\boldsymbol{R}_{ka}} \Psi_{p_{0i},nlm}(\Omega_i)(p_{0i}^2 + p^2)^{-1} \Psi^*_{p_{0i},N_1L_1M_1}(\Omega_i) \times [4\sin^2(\omega_i/2)]^{-1} e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}} \Psi^*_{p_{0i},n'l'm'}(\Omega'_i) \times (p_{0i}^2 + p'^2)^{-1} \Psi_{p_{0i},N'_1L'_1M'_1}(\Omega'_i)\, d\Omega_i\, d\Omega'_i. \tag{3.31}$$

(3) The integrals of two-electron exchange part

$$Q_3 = \int e^{i\boldsymbol{p}\boldsymbol{R}_{ka}} \Psi_{p_{0i},nlm}(\Omega_i) \Psi^*_{p_{0i},N_1L_1M_1}(\Omega_i)\, d\Omega_i \times \int e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}} \Psi^*_{p_{0i},n'l'm'}(\Omega'_i) \Psi_{p_{0i},N'_1L'_1M'_1}(\Omega'_i)\, d\Omega'_i. \tag{3.32}$$

It follows from the comparison with the integral (3.2) that the integral Q_3 can be expressed in terms of the integrals of S-type, namely

$$Q_3 = (2\pi^2)^2 S^{N_1L_1M_1a}_{nlmk} S^{n'l'm'k'}_{N'_1L'_1M'_1a'}. \tag{3.33}$$

The integral Q_2 can be easily reduced to a linear combination of integrals of Q_1-type. To perform this one can use Wigner–Biedenharn theorem about the expansion of a product of spherical harmonics in finite series in R_4.

Thus, it is necessary to calculate the integral of Q_1-type. There are at least two possible approaches here. The first one is to expand the kernel $[4\sin^2(\omega_i/2)]^{-1}$ in bilinear series of O(4)-harmonics. Then the integral has the form of infinite series of the functions S which are given by the Eq. (3.2). Such a series has absolute convergence, but for practical purposes the rate of this convergence is not sufficient since the integral Q_1 includes a sum over multipoles, i.e. over power functions of R^{-1}, the power function of distances R^{-1}_{ka} and $R^{-1}_{k'a'}$ being expanded in series of the functions of exponential decrease.

The second approach just provides the overcoming of this disadvantage, the expansion of the integral Q_1 being carried out in multipoles as well as exponentially decreasing functions of interatomic distances simultaneously.

So, let us consider the integral Q_1 given by the expression (3.30), and let us make the transformation from R_4-space to R_3-space by means of the Eq. (2.6) and following relations:

$$|\boldsymbol{p} - \boldsymbol{p}'|^{-2} = (2p_{0i})^2[(p_{0i}^2 + p^2)(p_{0i}^2 + p'^2)4\sin^2(\omega_i/2)]^{-1}, \quad d\Omega_i = [2p_{0i}/(p_{0i}^2 + p^2)]^3\, d^3\boldsymbol{p}. \tag{3.34}$$

Then

$$\Psi_{nlm}(\Omega_i)[4\sin^2(\omega_i/2)]^{-1}\Psi^*_{n'l'm'}(\Omega'_i)\,d\Omega_i\,d\Omega'_i$$
$$=(2p_{0i})^4 2^{-3}\pi^2 p_{0i}^{-5}\psi_{i,nlm}(\boldsymbol{p})\psi^*_{i,n'l'm'}(\boldsymbol{p}')|\boldsymbol{p}-\boldsymbol{p}'|^{-2}\,d^3\boldsymbol{p}\,d^3\boldsymbol{p}'. \tag{3.35}$$

Substituting the expression (3.35) into the integral (3.30) we can obtain the integral

$$Q_1 = 2p_{0i}^{-1}\pi^2 \int\int e^{i\boldsymbol{p}\boldsymbol{R}_{ka}}\psi_{i,nlm}(\boldsymbol{p})|\boldsymbol{p}-\boldsymbol{p}'|^{-2}$$
$$\times e^{-i\boldsymbol{p}'\boldsymbol{R}_{k'a'}}\psi^*_{i,n'l'm'}(\boldsymbol{p}')\,d^3\boldsymbol{p}\,d^3\boldsymbol{p}'. \tag{3.36}$$

With the help of the change of variables $\boldsymbol{p}-\boldsymbol{p}'=\boldsymbol{\eta}$ and the addition theorem for HAO (3.23) we can represent the integral Q_1 as the following sum:

$$Q_1 = 4(\pi p_{0i})^{1/2}2p_{0i}^{-1}\pi^2(-1)^{m'}\sum_{\nu\lambda\mu}(-1)^{\lambda}\int e^{i\boldsymbol{p}(\boldsymbol{R}_{ka}-\boldsymbol{R}_{k'a'})}$$
$$\times(p_{0i}^2+p^2)^{-1}\psi_{i,nlm}(\boldsymbol{p})\Psi_{p_{0i},\nu\lambda\mu}(\boldsymbol{p})\,d^3\boldsymbol{p}\times\sum_{\nu'\lambda'\mu'}G^{\lambda'\mu'}_{\lambda\mu;l'-m'}B^{\nu'\lambda'}_{n'l';\nu\lambda}$$
$$\times\int e^{-i\boldsymbol{\eta}\boldsymbol{R}_{k'a'}}\eta^{-2}\psi_{2p_{0i},\nu'\lambda'\mu'}(\boldsymbol{\eta})\,d^3\boldsymbol{\eta}. \tag{3.37}$$

Note that

$$Q_{NLM}(p_0,\boldsymbol{R})=\int e^{i\boldsymbol{\eta}\boldsymbol{R}}\eta^{-2}\psi_{p_0,NLM}(\boldsymbol{\eta})\,d^3\boldsymbol{\eta}. \tag{3.38}$$

The integral Q in Eq. (3.38) is a standard Coulomb integral which is worthy of consideration in detail.

When $\boldsymbol{R}=0$ we have

$$Q_{NLM}(p_0,0)=\int\eta^{-2}\psi_{p_0,NLM}(\boldsymbol{\eta})\,d^3\boldsymbol{\eta}$$
$$=\pi^2 N^{-1}p_0\psi_{p_0,NLM}(0). \tag{3.39}$$

When $\boldsymbol{R}\neq 0$ we have

$$Q_{NLM}(p_0,\boldsymbol{R})=2^{3/2}\pi^{-1}p_0^{5/2}b_{NL}\frac{(2L+2)_{N-L-1}}{(N-L-1)!}(2p_0)^L(p_0^2)^{N-L-1}$$
$$\times\bar{\mathcal{Y}}_{LM}(i\nabla_{\boldsymbol{R}})F(-N+L+1,-N+\tfrac{1}{2};L+\tfrac{3}{2};\Delta_{\boldsymbol{R}}/p_0^2)$$
$$\times\int\eta^{-2}e^{i\boldsymbol{\eta}\boldsymbol{R}}(p_0^2+\eta^2)^{-N-1}\,d^3\boldsymbol{\eta} \tag{3.40}$$

where the properties of Fourier integral are allowed for, while the polynomial part of the integrand is taken outside the integral and written in the form of polynomial differential operator acting on the parameter $\boldsymbol{R}$. The function $F(\alpha,\beta,\gamma,z)$ is the hypergeometric Gauss function reduced to Gegenbauer polynomial [8] (see also Eq. (3.13)). $\bar{\mathcal{Y}}_{LM}$ is the modified solid harmonic.

The calculation of the integral (3.40) can be reduced to Bessel transformation of a rational function. As a result we have

$$\int \eta^{-2} e^{-i\eta \boldsymbol{R}} (p_0^2+\eta^2)^{-N-1} d^3\eta = (-1)^N (N!)^{-1} 2\pi^2 R^{-1} D_{p_0^2}^N p_0^{-2} [1-\hat{k}_{1/2}(p_0 R)] \tag{3.41}$$

where $D_{p_0^2}^N = \partial^N/(\partial p_0^2)^N$, $\hat{k}_{1/2}(p_0 R)$ is the reduced Bessel function of half-integer index which is determined by the recurrent relation

$$z^2 \hat{k}_{N-1/2}(z) = \hat{k}_{N+3/2}(z) - (2N+1)\hat{k}_{N+1/2}(z) \tag{3.42}$$

with $\hat{k}_{-1/2}(z) = e^{-z} z^{-1}$, $\hat{k}_{1/2}(z) = e^{-z}$.

To calculate the integral (3.41) we represented the integrand fraction as the elementary fractions:

$$[\eta^2(p_0^2+\eta^2)]^{-1} = p_0^{-2}[\eta^{-2} - (p_0^2+\eta^2)^{-1}]. \tag{3.43}$$

Therefore, the integral (3.40) can be written as follows

$$\begin{aligned} Q_{NLM}(p_0, \boldsymbol{R}) = {} & 2^{3/2}\pi^{-1} p_0^{5/2} b_{NL} \frac{(2L+2)_{N-L-1}}{(N-L-1)!} (2p_0)^L (p_0^2)^{N-L-1} \\ & \times (-1)^N (N!)^{-1} 2\pi^2 \bar{\mathcal{Y}}_{LM}(i\nabla_{\boldsymbol{R}}) \\ & \times F(-N+L+1, -N+\tfrac{1}{2}; L+\tfrac{3}{2}; \Delta_{\boldsymbol{R}}/p_0^2) \\ & \times [R^{-1} D_{p_0^2}^N p_0^{-2} - R^{-1} D_{p_0^2}^N p_0^{-2} \hat{k}_{1/2}(p_0 R)]. \end{aligned} \tag{3.44}$$

One can easily obtain the result of the action of the operators $\bar{\mathcal{Y}}_{LM}(i\nabla_{\boldsymbol{R}})$ and $F(\cdots; \Delta_{\boldsymbol{R}}/p_0^2)$ on the function in the square brackets of Eq. (3.44), taking into account the following properties of the function:

$$\Delta_{\boldsymbol{R}} \frac{1}{R} = -4\pi\delta(\boldsymbol{R})$$

and

$$\bar{\mathcal{Y}}_{LM}(i\nabla_{\boldsymbol{R}}) R^{-1} = R^{-L-1} Y_{LM}(\hat{\boldsymbol{R}}) \hat{k}_{L+1/2}(0)$$

where

$$\hat{k}_{L+1/2}(0) = (2L)!(L!)^{-1} 2^{-L}$$

and

$$\Delta_{\boldsymbol{R}} \hat{k}_{-1/2}(p_0 R) = p_0^2 \hat{k}_{-1/2}(p_0 R) - 4\pi p_0^{-1} \delta(\boldsymbol{R}). \tag{3.45}$$

It follows from Eq. (3.45) that when $R \neq 0$

$$\begin{aligned} & F(-N+L+1, -N+\tfrac{1}{2}; L+\tfrac{3}{2}; \Delta_R/p_0^2) \hat{k}_{-1/2}(p_0 R) \\ & \quad = F(-N+L+1, -N+\tfrac{1}{2}; L+\tfrac{3}{2}; p_0^2/\bar{p}_0^2) \hat{k}_{-1/2}(p_0 R)|_{\bar{p}_0 = p_0} \end{aligned} \tag{3.46}$$

where we have introduced the parameter $\bar{p}_0$ to avoid a confusion with the differentiation parameter p_0. Further, from Eq. (3.45) we also have

$$\bar{\mathcal{Y}}_{LM}(i\nabla_{\boldsymbol{R}})\hat{k}_{-1/2}(p_0R) = p_0^{-1}R^{-L-1}Y_{LM}(\hat{\boldsymbol{R}})\hat{k}_{L+1/2}(p_0R). \tag{3.47}$$

So we obtain the following expression for the integral (3.40)

$$\begin{aligned} Q_{NLM}(p_0, \boldsymbol{R}) = (-1)^N 2^{5/2}\pi \frac{(2L+2)_{N-L-1}}{N!(N-L-1)!}(2p_0)^L (p_0^2)^{N-L-1} p_0^{5/2} \\ \times R^{-L-1}Y_{LM}(\hat{\boldsymbol{R}})[\hat{k}_{L+1/2}(0)D_{p_0^2}^N p_0^{-2} \\ - D_{p_0^2}^N p_0^{-2} F(-N+L+1, -N+\tfrac{1}{2}; L+\tfrac{3}{2}; p_0^2/\bar{p}_0^2)\hat{k}_{L+1/2}(p_0R)] \end{aligned} \tag{3.48}$$

where $\bar{p}_0 = p_0$ is meant.

It is not difficult to carry out the remaining differentiation with respect to p_0^2, if one takes into account the fact that Gauss function F is a polynomial of the degree of $N-L-1$.

Finally the substitution of the following expressions for the derivatives:

$$D_{p_0^2}^N p_0^{-2} = (-1)^N N!(p_0^{-2})^{N+1} \tag{3.49a}$$

and

$$\begin{aligned} D_{p_0^2}^N p_0^{-2} F(-N+L+1, -N+\tfrac{1}{2}; L+\tfrac{3}{2}; p_0^2/\bar{p}_0^2)\hat{k}_{L+1/2}(p_0R)|_{\bar{p}_0=p_0} \\ = \sum_t^{N-L-1} \binom{N}{t} p_0^{-2t} \frac{(-N+L+1, t)(-N+\tfrac{1}{2}, t)\Gamma(L+t+\tfrac{3}{2})\Gamma(2N-t)}{(L+\tfrac{3}{2}, t)\Gamma(N+\tfrac{1}{2})\Gamma(N+L+1)} \\ \times \Bigg[\sum_{s=0}^{L} (-1)^s \binom{N-t}{s} 2^{-s} R^{2s} \hat{k}_{L+1/2-s}(p_0R) \\ + \sum_{s=L+1}^{N-t} (-1)^s \binom{N-t}{s} 2^{-s} p_0^{-2s+2L+1} R^{2L+1} \hat{k}_{s-L-1/2}(p_0R) \Bigg] \end{aligned} \tag{3.49b}$$

into the Eq. (3.48) yields a standard working formula for Coulomb integral $Q_{NLM}(p_0, \boldsymbol{R})$.

It follows from Eq. (3.48) that the Coulomb integral includes both the multipole contribution which is regular at large distances R, and the contribution with exponential decrease.

Therefore the mathematical structure of the expression (3.48) leads to the physically important result concerning the predominance of multipole contributions to Coulomb integrals at large inter-atomic distances R.

Returning to the integral Q_1 (3.37) we can see that the integral over $d^3\boldsymbol{p}$ which remained uncalculated coincides up to a coefficient with the function (3.2)

wherein $\boldsymbol{R}_{kk'}$ should be replaced by $\boldsymbol{R}_{ka}-\boldsymbol{R}_{k'a'}$, namely

$$\int e^{i\boldsymbol{p}(\boldsymbol{R}_{ka}-\boldsymbol{R}_{k'a'})}(p_{0i}^2+p^2)^{-1}\psi_{p_{0i},nlm}(\boldsymbol{p})\Psi_{p_{0i},\nu\lambda\mu}(\boldsymbol{p})\,d^3\boldsymbol{p}$$

$$=(-1)^{\mu}2^{5/2}\pi p_{0i}^{5/2}(2p_{0i})^{-3}S_{nlm}^{\nu\lambda-\mu}(\boldsymbol{R}_{ka}-\boldsymbol{R}_{k'a'}). \tag{3.50}$$

Finally we have

$$\begin{aligned}Q_1=&(-1)^{m'}2^{5/2}\pi p_{0i}^{5/2}4(\pi p_{0i})^{1/2}2^7p_{0i}^{-1}\pi^{-2}\\&\times\sum_{\nu\lambda\mu}(-1)^{\mu+\lambda}S_{nlm}^{\nu\lambda-\mu}(p_{0i},\boldsymbol{R}_{ka}-\boldsymbol{R}_{k'a'})\\&\times\sum_{\nu'\lambda'\mu'}G_{\lambda\mu;l-m'B_{n'l';\nu\lambda}}^{\lambda'\mu'}Q_{\nu'\lambda'\mu'}(2p_{0i},\boldsymbol{R}_{k'a'})\end{aligned} \tag{3.51}$$

where the substitutions $p_{01}=p_{0i}, p_{02}=p_{0i}$ and $p_0=2p_{0i}$ should be done to calculate the coefficients B.

Putting $a=a'$ we obtain the expression for one-electron Coulomb contribution to the matrix element H (3.22).

At last let us consider the integral of Q_2-type (3.31). It differs from Q_1 (3.30) by the presence of the product of two harmonics of O(4) instead of $\Psi_{nlm}(\Omega_i)$. Let us use Wigner–Biedenharn theorem and represent the product of 4-dimensional spherical harmonics in the form of their finite sum:

$$\Psi_{nlm}(\Omega)\Psi_{\nu\lambda\mu}(\Omega)=\sum_{NLM}C(nlm,\nu\lambda\mu;NLM)\Psi_{NLM}(\Omega) \tag{3.52}$$

where coefficients $C(nlm,\nu\lambda\mu;NLM)$ are given by the integral (3.7). Further let us take into consideration that

$$(p_0^2+p^2)^{-1}=(2p_0)^{-2}2(1+\cos\alpha)=(2p_0)^{-2}[2\Psi_{100}(\Omega)+\Psi_{200}(\Omega)]. \tag{3.53}$$

Making use of Eqs. (3.52) and (3.53) we can transform the integral (3.51) to the following sum of integrals of Q_1-type:

$$\begin{aligned}Q_2=&(-1)^{M_1'+M_2}(2p_{0i})^{-4}\\&\times\sum_{v=1}^{2}d_v\sum_{v_1}C(v00,N_1L_1-M_1;v_1L_1-M_1)\\&\times\sum_{N_2L_2M_2}C(nlm,v_1L_1-M_2;N_2L_2M_2)\\&\times\sum_{v'=1}^{2}d_{v'}\sum_{v_1'=1}C(v'00,N_1'L_1'-M_1';v_1'L_1'-M_1')\\&\times\sum_{N_2'L_2'M_2'}C(n'l'm',v_1'L_1'-M_2';N_2'L_2'M_2')\\&\times Q_1(N_2L_2M_2,N_2'L_2'M_2';p_{0i},\boldsymbol{R}_{ka},\boldsymbol{R}_{k'a'}),\end{aligned} \tag{3.54}$$

where $d_1=2$, $d_2=1$.

To complete the calculation of the matrix element of H (3.22) we should evaluate the integrals over $d^3\eta$ in Eqs. (3.28) and (3.29). This procedure is quite simple. Indeed, one can reduce the integral in Eq. (3.28) to the functions of Eq. (3.2)-type if one transforms the momentum η to the spherical coordinates of R_4-space.

$$\int \psi^*_{p_0,N_2L_2M_2}(\eta)\psi_{p_0,N_2'L_2'M_2'}(\eta)\, e^{i\eta R}\, d^3\eta$$

$$= (\pi^{-1}2^{3/2}p_0^{5/2})^2(2p_a)^{-5}2\pi^2 \sum_{v=1}^{2} d_v$$

$$\times \sum_{v'} C(v00, N_2'L_2'M_2'; v'L_2'M_2')S^{N_2L_2M_2}_{v'L_2'M_2'}(\boldsymbol{R}). \tag{3.55}$$

The integral in Eq. (3.29) can be reduced to an integral of Q-type by means of Wigner–Biedenharn theorem with allowance made for the relation

$$(2p_0)^4(p_0^2+p^2)^{-2} = \sum_{v=1}^{3} d_v'\Psi_{v00}(\Omega) \tag{3.56}$$

where $d_v' = \{5, 4, 1\}$.

As a result we obtain the desired expression for Coulomb integral in Eq. (3.29):

$$\int e^{i\eta R}\eta^{-2}\psi^*_{p_0,N_2L_2M_2}(\eta)\psi_{p_0,N_2'L_2'M_2'}(\eta)\, d^3\eta$$

$$= \pi^{-1}2^{3/2}p_0^{5/2}(2p_0)^{-4}(-1)^{M_2} \sum_{v=1}^{3} d_v'$$

$$\times \sum_{v_1} C(v00, N_2'L_2'M_2'; v_1L_2'M_2')$$

$$\times \sum_{N_3L_3M_3} C(N_2L_2-M_2, v_1L_2'M_2'; N_3L_3M_3)Q_{N_3L_3M_3}(p_0, \boldsymbol{R}). \tag{3.57}$$

4. Summary

We have calculated all the matrix elements for the given theory of the solution of integral Hartree–Fock equations by the method of MO LCAO for many-atomic molecules. We have showed that the matrix elements can be expressed in the form of expansions in standard functions such as overlap integrals $S(\boldsymbol{R})$ and one-electron Coulomb integrals $Q(\boldsymbol{R})$ which depend on inter-atomic distances. Since the present theory of solution of integral Hartree–Fock equations does not include any semi-empirical parameter, it can be used to carry out rather precise *ab initio* calculations of electronic molecular terms (naturally, in the frame of restricted precision of Hartree–Fock theory). In this work we did not consider the problem of correlations in calculations of the electronic terms. This is a subject of a special investigation.

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