Atoms and molecules in relativistic quantum mechanics

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Abstract. Relativistic N-electron Hamiltonian can be written as a sum of the one electron Dirac Hamiltonians for an electron moving in the external field of nucleus, the Coulomb repulsion potential energy between electrons and the Breit operator representing the magnetic and retardation corrections to this interaction. Approximating many-electron wave function by a sum of anti-symmetrised products of orthonormal single particle spinors and using it as a trial function in a variational method leads to the Dirac-Fock equations for N-electron system. However the presence of a continuum of negative energy states below the bound states in the spectrum of Dirac Hamiltonian is a source of a several difficulties in atomic and molecular structure calculations: the Brown-Ravenhall disease, variational collapse and variational prolapse. Taking the boundary conditions properly into account, imposing the kinetic balance condition for small and large component basis sets, using correct strategy in developing basis sets and employing the finite nuclear size model results in the workable finite-difference and the basis-set methods of calculation for relativistic atomic and molecular structure.

1. Introduction
It is well known that an accurate theoretical determination of properties for systems containing heavy elements requires inclusion of relativistic effects in electronic structure calculations. There are many approximate methods of treating relativity. All of them can be derived from the many-electron Dirac-Coulomb-Breit equation. Attempts to set up relativistic SCF calculations for atoms were initiated by Swirles in 1935 [1]. Then, after fundamental paper of Grant in 1970 [2], the program of Desclaux (1975) [3] and programs of the group of Grant (1980, 1989) [4,5] were published, which allowed for relativistic SCF calculations for atomic systems. A closed-shell molecular DF formalism in which 4-component atomic spinors were used as basis set functions was first proposed by Malli in 1975 [6]. However, codes which exploit the so-called kinetic balance condition, to prevent the variational collapse, were developed in 1980/1990. Two of them, MOLFDIR [7] and DIRAC [8] became nowadays standard tools in relativistic electronic structure calculations for molecules.

2. One-particle Dirac equation
The hydrogen-like atom in the Dirac theory is modeled by an electron moving in an external Coulomb field. Then corresponding equation describing the electron can be written as:

\[
\begin{pmatrix}
V & c\sigma \cdot \hat{p} \\
-2mc^2 & V - 2mc^2
\end{pmatrix}
\begin{bmatrix}
\psi^i \\
\psi^j
\end{bmatrix}
= \epsilon
\begin{bmatrix}
\psi^i \\
\psi^j
\end{bmatrix},
\]

(1)

where \(\sigma = (\sigma_x, \sigma_y, \sigma_z)\) is the vector of the Pauli matrices and \(\hat{p} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)\) is the momentum operators vector. \(V = -\frac{Ze^2}{r}\) is the potential energy of interaction of electron with nucleus, \(c\) is the speed.
of light and $\psi^L$, $\psi^S$ are the large and small components of the 4-component spinor, respectively. The physical interpretation of this equation can be found in standard textbooks [9,10] and only some important point will be summarized here. The spectrum of such Hamiltonian is unbounded from above and from below. It consist of two continua ($\varepsilon > 0$, $\varepsilon < -2mc^2$) and the discrete part (bound electron states) located below positive energies continuum. It is presented in the figure 1. The negative-energy solutions ($E < 0$) may be interpreted as solutions for particles with charge $+e$, positrons, while the positive energy solutions ($E > 0$) as a solutions for particles with charge $-e$, electrons.

Figure 1. Spectrum of the Dirac Hamiltonian for the hydrogen-like atom ($\varepsilon = E - mc^2$)

From the second of equations (1) we can express the small component $\psi^S$ as a function of the large component $\psi^L$:

$$\psi^S = (2mc^2 + \varepsilon - V)^{-1} c\sigma \cdot \hat{p} \psi^L.$$  \hspace{1cm} (2)

Then, after substituting it to the first of equations (1) we will obtain:

$$V\psi^L + \sigma \cdot \hat{p} \left[ 2m \left( 1 + \frac{\varepsilon - V}{2mc^2} \right)^{-1} \right] \sigma \cdot \hat{p} \psi^L = \varepsilon \psi^L.$$  \hspace{1cm} (3)

If we assume that the speed of light $c \to \infty$ (the nonrelativistic limit) and notice that $(\sigma \cdot \hat{p})(\sigma \cdot \hat{p}) = \hat{p}^2$, the above equation reduces to a two-component Schrödinger equation:

$$V\psi^L + \frac{1}{2m} \hat{p}^2 \psi^L = \varepsilon \psi^L.$$  \hspace{1cm} (4)

We can also expand the eigenfunctions of the Dirac Hamiltonian in a basis set of 2-spinors $\chi^L_i$ and $\chi^S_j$:

$$\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \sum_{i=1}^{N_L} c^L_i \begin{pmatrix} \chi^L_i \\ 0 \end{pmatrix} + \sum_{j=1}^{N_S} c^S_j \begin{pmatrix} 0 \\ \chi^S_j \end{pmatrix}. \hspace{1cm} (5)$$

Substituting the above expansion into equations (1) leads to the matrix representation of the Dirac equation:

$$\begin{pmatrix} V^{LL} & c(\sigma \cdot \hat{p})^{LS} \\ c(\sigma \cdot \hat{p})^{SL} & V^{SS} - 2mc^2 S^{SS} \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \varepsilon \begin{pmatrix} S^{LL} & 0 \\ 0 & S^{SS} \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}.$$  \hspace{1cm} (6)
where \( V_{ij}^{XX} = \int \chi_i^X \chi_j^X d\tau \), \( S_{ij}^{XX} = \int \chi_i^X \chi_j^X d\tau \) and \( \pi_{ij}^{XY} = \int \chi_i^X \cdot \hat{p} \chi_j^X d\tau \), \( X, Y = L, S \). From the second of equations (6) we can derive a relation connecting the expansion coefficients for a small and large component functions:

\[
\mathbf{c}^S = \frac{1}{2mc} \left[ S^{SS} + \frac{1}{2mc^2} (\mathbf{c} S^{SS} - S^{VV}) \right]^{-1} (\mathbf{c} \cdot \hat{\mathbf{p}})^{SL} \mathbf{c}^L.
\]

Substituting it into first of equations (6) we will obtain:

\[
\left\{ \mathbf{V}^{LL} + \frac{1}{2m} (\mathbf{c} \cdot \hat{\mathbf{p}})^{LS} \left[ S^{SS} + \frac{1}{2mc^2} (\mathbf{c} S^{SS} - S^{VV}) \right]^{-1} (\mathbf{c} \cdot \hat{\mathbf{p}})^{SL} \right\} \mathbf{c}^L = \mathbf{c} S^{LL} \mathbf{c}^L.
\]

Again, if we assume the speed of light \( c \to \infty \) and if

\[
(\mathbf{c} \cdot \hat{\mathbf{p}})^{LS} \left[ S^{SS} \right]^{-1} (\mathbf{c} \cdot \hat{\mathbf{p}})^{SL} = \left[ p^2 \right]^{LL},
\]

we obtain a matrix representation of the Schrödinger equation. However the relation (9) is true only, if the resolution of the identity is fulfilled for the basis set [11]. It can be established only, if the functions satisfy the relation (2) between small and large component [12], which in approximate form (we neglect V and \( \varepsilon \) because these are small relative to \( 2mc^2 \)) can be written as:

\[
\chi^l = \frac{1}{2mc} \hat{\mathbf{p}} \chi^L.
\]

This relation for basis functions of large and small component is called kinetic balance condition. If for a chosen basis condition this condition is not fulfilled, the obtained values of the kinetic energy are too small and convergence to nonrelativistic limit upon enlarging the value of \( c \) will not take a place. The effect of operator \( \hat{\mathbf{p}} \) on the spatial part of large component function is determined by the differential operators \( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \). For example, the result of action of \( \frac{\partial}{\partial x} \) on a primitive scalar Gaussian function is

\[
\frac{\partial}{\partial x} \chi^l \exp(-\zeta r^2) = \left(l\zeta x^l - 2\xi x^l\right) \exp(-\zeta r^2),
\]

i.e. we have obtained linear combination of two functions with the same value of exponent \( \zeta \), but with different values of \( l \). To fulfill the kinetic balance condition these functions should be included in the small component basis set either as two separate functions or as a linear combination of two functions. In the relativistic theory we solve the Dirac equation with the potential energy of point nucleus, \( V = -\frac{Ze^2}{r} \). Both large and small components of radial wavefunctions may be expressed as products of \( \exp(-\zeta r) \) and a polynomial of \( r \). At the origin it behaves as \( r^{\gamma-1} \), which for \( \gamma = \pm 1 \) is singular since the value of \( \gamma = \sqrt{\kappa^2 - (Ze^{-1})^2} \) is less than 1. The basis functions are usually chosen to resemble the solutions of the hydrogen-like atom. This weak singularity at the origin for \( 1s_{\nu_2} \) and \( 2p_{\nu_2} \) is a consequence of the point nucleus potential and is difficult to describe with a Slater or Gaussian functions. If a more physical, finite model of the nucleus is used, it disappears and the radial wavefunction at the origin becomes Gaussian like. The most popular models of nuclear charge distribution used in atomic structure calculations are the uniform charge distribution model (UN):

\[
\rho_{\text{nucl}}(r) = \begin{cases} \rho_o, & r \leq r_o \\ 0, & r > r_o \end{cases},
\]

and the Fermi distribution (FN):
\[
\rho_{\text{nuc}}(r) = \frac{\rho_o}{1 + \exp \left( \frac{r - r_o}{t} \right)} \tag{13}
\]

In molecular calculations usually we are trying to describe accurately the region of chemical bonding and the valence electrons involved in it and therefore we may choose the model of finite nucleus which is convenient to use from the point of view of simplicity of calculations. Therefore very often a Gaussian distribution function of the nuclear charge (GN) is used:

\[
\rho_{\text{nuc}}(r) = \rho_o \exp \left( -\eta_o r^2 \right). \tag{14}
\]

These models are a crude representation of the nuclear charge distribution, sufficient for electronic structure calculations. The parameters \( r_o, t, \eta_o \) of these models are determined from the fitting of nuclear scattering data to obtain gross nuclear dimensions [13].

3. N-electron systems

Totally covariant Hamiltonian for a system of interacting particles does not exist and the approximate form of it is inherent in a relativistic theory. Usually it is written as a sum of one-electron Dirac Hamiltonians \( \hat{H}^D(i) \) and a sum of operators \( \hat{G}(i, j) \) describing the electron-electron interaction. In the formalism of QED the electron-electron interaction is represented by the exchange of virtual photons. Series expansion of the complete interaction of two electrons gives the Coulomb interaction as a first term (proportional to \((Z\alpha)^0\)) and the Breit interaction as a second (proportional to \((Z\alpha)^2\)), where \( \alpha \) is the fine structure constant. In this way the invariance correction to the Coulomb interaction is added and the approximate relativistic N-electron Hamiltonian can be written as a Dirac-Coulomb-Breit (DCB) Hamiltonian:

\[
\hat{H}^{DCB} = \sum_{i=1}^{N} \hat{H}^D(i) + \sum_{i<j}^{N} \left[ \frac{e^2}{r_{ij}} + \hat{B}(i, j) \right], \tag{15}
\]

where

\[
\hat{H}^D(i) = c\hat{\alpha}_i \cdot \hat{p}_i + mc^2(\beta_i - 1) + V(i) \text{ is the Dirac Hamiltonian of electron } i \text{ in the external field of clamped nuclei,}
\]

\( \hat{\alpha}_i, \hat{\beta}_i \) are the \( 4 \times 4 \) Dirac matrices of electron \( i \),

\( e, m \) – represent charge and rest mass of electron, respectively,

\( c \) – is the speed of light,

\( \frac{e^2}{r_{ij}} \) – is the potential energy of Coulombic repulsion of electrons \( i \) and \( j \).

The Breit operator can be written in the form:

\[
\hat{B}(i, j) = -\frac{e^2}{2} \left( \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{r_{ij}} + \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{r_{ij}^3} \right), \tag{16}
\]

and can be interpreted as a sum of magnetic interaction of two Dirac currents

\[
\hat{B}^G(i, j) = -\frac{e^2}{r_{ij}} \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{r_{ij}}, \tag{17}
\]

and the retardation correction to interaction of two electrons

\[
\hat{B}^{ret}(i, j) = \frac{e^2}{2r_{ij}} \left( \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{r_{ij}^3} - \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{2r_{ij}^3} \right). \tag{18}
\]
If the Breit operator is not taken into account in the considerations, the N-electron Hamiltonian consists of the sum of one-electron Dirac Hamiltonians and the nonrelativistic coulombic repulsions between electrons and is called in the literature the **Dirac-Coulomb (DC) Hamiltonian**.

Let us consider for a while the **independent –particle model**. Even for non-interacting particles the approximate N-electron function should be antisymmetric with respect to a transposition of two electrons and should fulfill the Pauli exclusion principle. The anti-symmetrised product of orthonormal single particle 4-component spinors $\psi$ (*Slater determinant*) defined as

$$
\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(1) & \psi_1(2) & \ldots & \psi_1(N) \\
\psi_2(1) & \psi_2(2) & \ldots & \psi_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_N(1) & \psi_N(2) & \ldots & \psi_N(N)
\end{vmatrix}
$$

fulfills both conditions. For non-interacting particles the eigenvalue problem may be separated into N independent one-electron eigenvalue problems. In the relativistic case however, the energy of N-electron state is degenerate with an infinite number of continuum states. For example, in case of N = 2 we obtain the energy $E = \varepsilon_1 + \varepsilon_2$, which correspond to a Slater determinant build from two spinors corresponding to one-electron energies $\varepsilon_1$ and $\varepsilon_2$. However, the same energy will be obtained for two orbital energies $\varepsilon_1 + mc^2 + \delta$ and $\varepsilon_2 - mc^2 - \delta$ ($\delta > 0$) belonging to a positive and negative continuum energy, respectively [14,15]. This property of the Dirac spectrum is known as the **Brown-Ravenhall disease**. One-electron eigenvalue problems are exactly solvable and for a non-interacting electrons one can easily separate many-electron discrete states from the continuum ones by building the Slater determinant from those one-electron spinors which correspond to the discrete values of one-electron energies. However, the eigenvalue problem for DCB Hamiltonian can be solved only using approximate methods and one has to be careful to avoid the contaminations of the spinors from the continuum states. The many electron DCB Hamiltonian is unbound from below and the true N-electron solutions represent local minima that lie above a continuum of states in which one or more electrons occupy positron-like states [12]. In order to apply the variational method to solve the DCB eigenvalue problem we can transform the DCB Hamiltonian into operator which is bounded from below but the formalism become very complicated. In another approach we restrict the space of the trial functions by imposing the boundary conditions, which would force trial functions to be orthogonal to the negative-energy solutions [14]. The approach in which the contributions of states with electron-positron pairs are neglected is called the **no-pair approximation**.

### 3.1 Atomic systems

In case of closed shell atom an atomic state function $\Phi_{\alpha}(JM)$ for a ground state $\alpha$ is a single Slater determinant constructed from central-field Dirac spinors:

$$
\psi_{\alpha}(r) = \frac{1}{\sqrt{\Omega}} \sum_{nk\\m} P_{nk}(r) Q_{\alpha mk}(\hat{r}),
$$

where $P, Q$ are the large and small radial components of spinor and $\Omega$ is the spin-angular function constructed according to the rules of coupling the angular momenta. The radial wavefunctions with a given value of kappa form an orthonormal set, i.e.:
The energy of state $\alpha$ is given by

$$E_\alpha = \int \Phi_\alpha^\dagger (JM) \hat{H} \Phi_\alpha (JM) d\tau.$$  

By requiring that this energy functional should be stationary when subject to variations in the radial wavefunctions $P$ and $Q$ with the condition that the orbitals form an orthonormal set, we will obtain the Dirac-Fock (DF) equations (in atomic units $m = e = \hbar = 1$) for an orbital $\alpha$ ($a \equiv (n, \kappa, m)$):

$$\frac{dP_a}{dr} + \kappa_a \frac{P_a}{r} - \left(2e - \frac{e_a}{c} + \frac{Y_a}{cr} \right) Q_a = -\frac{1}{r} \left( X_a^{(P)} + \frac{r}{c\epsilon_a} \sum_{b\neq a} \epsilon_{ab} Q_b \right),$$

$$\frac{dQ_a}{dr} - \kappa_a \frac{Q_a}{r} + \left( \frac{e_a}{c} + \frac{Y_a}{cr} \right) P_a = -\frac{1}{r} \left( X_a^{(Q)} - \frac{r}{c\epsilon_a} \sum_{b\neq a} \epsilon_{ab} P_b \right),$$  

where $Y_a(r)$, $X_a^{(P,Q)}$ are direct and exchange potentials, respectively, $\epsilon_{ab}$ are the Lagrange multipliers, $\bar{q}_a$ are the generalized occupation numbers for spinor $a$ [4]. These radial Self-Consistent-Field (SCF) equations may be integrated by finite difference method. In the numerical procedure we request the proper boundary conditions which allows for a clear separation of bound electronic states and continuum energy states:

$$P_n^{\kappa_a}(r = 0) = 0, \quad P_n^{\kappa_a}(r \rightarrow \infty) \rightarrow 0, \quad P_n^{\kappa_a}(r \rightarrow 0) > 0,$$

$$Q_n^{\kappa_a}(r = 0) = 0, \quad Q_n^{\kappa_a}(r \rightarrow \infty) \rightarrow 0.$$  

This way we can avoid the variational collapse problem, when obtained energy of a system is much below the exact value.

### 3.2 Molecular systems

The N-electron wavefunction for a closed shell molecule can be written as a single Slater determinant. The one electron spinors the determinant is build from, should be taken to belong to the positive-energy part of an appropriate single particle spectrum. With this choice the DC and DCB Hamiltonians are truncated and bounded from below [7] and the contributions of the states with electron-positron pairs are neglected (no-pair approximation). However, the division of the one-particle space into a positron (negative energy) and an electron (positive energy) part depends on the potential $V$, which in case of SCF methods changes during the process of optimization of the occupied spinors. In case of a molecule, because of the lack of spherical symmetry, we can not separate the equation into an angular and radial part. In such a case the number of grid points used in a numerical integration method is becoming extremely large, which make the numerical integration of the SCF equations practically impossible. Therefore, we have to use a basis set approach in which one-electron spinors are written as a linear combinations of a finite number of known (usually Gaussian type) functions. Similarly like in one-electron case, we expand separately the large and small components of the 4-component spinors in a basis of 2-spinors $\chi_{\mu}^L$ and $\chi_{\nu}^S$:

$$\psi_j^L = \sum_{\mu=1}^{N_L} c_{\mu j}^L \chi_{\mu}^L, \quad \psi_j^S = \sum_{\nu=1}^{N_S} c_{\nu j}^S \chi_{\nu}^S.$$  

Inserting these expansions into the energy functional and requiring its minimum with respect to the variation of one electron spinors leads to the Dirac-Fock equations in an algebraic approximation.
The expressions for the elements of the various blocks of the Fock matrix can be found in [17]. The Dirac spinors have to fulfill very strict boundary conditions in order to prevent the variational collapse. Particularly important are the correct behavior of the spinors at the nuclei and correct relations between large and small components of the Dirac spinors [13,14], the kinetic balance condition (10). Since the separation between the positive- and negative-energy spinors is not established until the Dirac-Fock equations are solved, the search for the local minimum during the SCF procedure could encounter the convergence problems. In practice however, the energy eigenvalues of the two types of solutions are so far apart, that their mixing is weak. Convergence of the SCF process is usually smooth with the energy expectation value approaching the stationary value from above [7].

In case of the basis set expansion method, the variational collapse results in a calculated DF total energy for given system lower than the corresponding numerical DF energy. If the basis set exploited in calculations, fulfills the kinetic balance condition, the collapse in principle will not appear. However Faegri [18] noticed that for some basis sets with the proper relation between the small and large components, a small variation collapse will appear and named it prolapse. The exponents ζ of the functions belonging to a given basis set are very often chosen to minimize the DF energy, i.e. the exponents are used as variational parameters (so called energy-minimized basis sets). The size of basis arise as a compromise between maximum flexibility and minimum cost of calculations. Talman [19] showed, that the DF energy represent a minimum in the space of variational parameters for the positive energy states, but a maximum in the variational space for the negative energy states:

\[
E[\Phi] = \min_{\{H_L|H_S\}} \frac{\langle \Phi | H^{DC} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \tag{28}
\]

The coupling of the exponents for the large and small components (the kinetic balance condition) provides an implicit projection onto the positive energy states. However, in a truncated basis set this projection only approximates the real energy surface spanned by the orbital rotations and the minimum found during the exponent optimization process may correspond to the energy below the numerical value [18]. This is not a collapse of the variational process observed when kinetic balance condition is not obeyed, but it is the result of incompleteness of the basis set and is called prolapse. The improving of the valence space by adding more s and p functions in the minimization process may lead to an unrealistic saturation of the inner function space and result in the DF energy value below the corresponding numerical value. One way to avoid this is to freeze the inner function, when core orbitals are sufficiently well described, the other is just to be restrictive with the size of the s and p sets.

An efficient use of the symmetry of a system can help to keep the DF calculations feasible. To achieve this goal, the basis functions are constructed to transform according to the irreducible representations of the point group symmetry of the molecule. Additionally, the Kramers (time-reversal) symmetry can be utilized. This symmetry cause the twofold degeneracy of all spinor eigenvalue of a system (in the absence of external magnetic field). The time-reversal operator commutes with the DCB Hamiltonian and is defined as:

\[
\hat{K}_4 = -i \begin{bmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{bmatrix} \hat{K}, \tag{29}
\]

where \( \hat{K} \) is the complex conjugation operator.

Operating with \( \hat{K}_4 \) on a given spinor \( \psi_i \) gives another spinor \( \psi'_i \) with the same eigenvalue. The contribution of both spinors to the SCF-density matrix will be the same, but occur at a different place. This relation makes it possible to reduce the CPU and memory requirement by a factor 2 [12].
4. Examples of calculations

Many relativistic all electron 4-component calculations for heavy and super heavy element systems have been published within the last 15 years, for example the calculations for hydrogen halides series (up to astatine atom with Z = 85) [20,21] and Rutherfordium tetrachloride molecule RfCl$_4$ (Z = 104 for Rf) [22]. We will discuss here shortly the calculations for the uranium atom (Z = 92) and for the molecule of uranium hexafluoride (UF$_6$) of O$_h$ symmetry [23,24]. In table 1 the energies of chosen spinors and total ground state energy of the uranium atom obtained using Hartree-Fock and Dirac-Fock methods are presented.

Table 1. The values (in a.u.) of the orbital energies and the energy of average of configurations for the uranium atom obtained using algebraic HF and DF methods. In the last column the differences of relativistic and nonrelativistic energies (in eV) are given.

| $nl_j$ | DF(a.u.) | HF(a.u.) | $\Delta^{rel}$(eV) |
|--------|----------|----------|---------------------|
| $1s_{1/2}$ | -4278.1065 | -3716.1152 | -15292.57 |
| $2s_{1/2}$ | -805.9781 | -650.8961 | -4220.00 |
| $2p_{1/2}$ | -776.1816 | -629.0471 | -4003.74 |
| $2p_{3/2}$ | -635.5900 | -629.0471 | -178.04 |
| $6s_{1/2}$ | -2.1378 | -1.6820 | -12.40 |
| $6p_{1/2}$ | -1.3443 | -1.0360 | -8.39 |
| $6p_{3/2}$ | -0.9865 | -1.0360 | 1.35 |
| $5f_{5/2}$ | -0.3494 | -0.6349 | 7.77 |
| $5f_{7/2}$ | -0.3219 | -0.6349 | 8.52 |
| $6d_{3/2}$ | -0.1925 | -0.2652 | 1.98 |
| $6d_{5/2}$ | -0.1829 | -0.2652 | 2.24 |
| $7s_{1/2}$ | -0.2025 | -0.1667 | -0.97 |
| $E_{TOT}$ | -28048.97995 | -25662.61782 | -64936.2442 |

In the last column of this table the relativistic corrections to the spinor and total energies calculated as a difference of the corresponding DF and HF energies are displayed. One can see that the relativity lowers significantly the values of spinor energies of the core electrons. This effect for $1s_{1/2}$ orbital is about 15300 eV. The lowering of the total energy is huge, i.e. 65000 eV. In case of spinors with $l > 0$ we observe the spin-orbit splitting for $j = l - 1/2$ and $j = l + 1/2$. This effect is large even for valence spinors, the value of the splitting for $2p$ orbital is 3825 eV, while for the $6p$ orbital it is 10 eV. The relativistic effects change substantially the values of the spinor energies and the energetic distances between the spinors. It influence the interpretation of the atomic spectrum of the U atom, as well as the description and mechanism of the bonding between U and surrounding F atoms in the UF$_6$ molecule. The molecular spinors energies obtained within relativistic approach differ from corresponding HF values. The ordering and energetic distances between the molecular spinors have been changed drastically compared to nonrelativistic results. The highest occupied molecular orbital (HOMO) obtained in HF calculations which has partially $s_{1/2}$ character, shifts down in energy due to the contraction of the uranium $s_{1/2}$ and $p_{3/2}$ shells. The large spin orbit splitting of the next orbital below HOMO can be explained by its significant U6p character, while the splitting of atomic U6p orbital is about 10 eV. The dissociation energy $D_e$ calculated for the UF$_6$ molecule using HF method is 9 eV, while the corresponding value obtained using DF method is 23 eV.
5. Conclusions
The relativistic all electron 4-component numerical and algebraic Dirac-Fock methods for atoms and molecules are well established. Understanding the role of boundary conditions, i.e. the behavior of the spinors in the origin and for \( r \to \infty \) as well as the kinetic balance condition, exploiting the model of finite nucleus and using the correct strategy in developing the basis sets, made it possible to develop numerical and algebraic Dirac-Fock methods for atoms and molecules. This methods were implemented in computer programs and become the standard tools for physicists and chemists, who study the electronic structure of atomic and molecular N-electron systems. All electron relativistic 4-component calculations for systems containing heavy and very heavy elements with hundreds of electrons are feasible. The most recent review of 4-component method and calculations can be found in [25] and [26].

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