

A Relativistic Virtual Orbital Obtained from a Discrete Basis Set

A.L.A. FONSECA

Departamento de Física, Universidade de Brasília, 70910, Brasília, DF, Brasil

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Abstract We present a method to obtain a relativistic virtual orbital, which makes use of a discrete basis set. We use this virtual orbital in multiconfigurational calculations with mixtures of five configurations $sp + \tilde{d}$ for $j = 1$, in order to obtain the hyperfine electronic constant $(r^{-3})^{\mu\nu}$ with $\mu\nu = 10, 01, 12, 02$ (using the effective operator) of the 3P_1 level of calcium and the hyperfine (HFS) constant $A(^3P_1)$ of barium.

1. INTRODUCTION

Optical spectra of alkaline-earth atoms are much more complicated than expected: the two outermost electrons in closed subshells are rather loosely bound, therefore they are strongly affected by correlation.

The Hartree-Fock (HF) method is not capable to give correct results^{1,2} due to the quasi-degeneracy of the ns and $(n-1)d$ orbitals. On the other hand the Multi-Configurational Hartree-Fock (MCHF) method has been successfully applied in energy level determination³, in the interpretation of Strontium atom⁴ isotope shifts, in refined evaluations of field isotope shifts and in the hyperfine structure of the calcium atom⁵.

Our experience with MCHF calculations^{3,4} suggests that in order to achieve convergence it is essential to start with a reasonable approximation for the *virtual* or *correlated* orbital as input for the Froese Fischer's code⁶. This approximation was obtained through the use of Labarthe's code⁷.

The configuration mixing plays a very important role in the determination of atomic parameters. The relativistic Desclaux's code⁸ for the Multiconfigurational Dirac-Fock (MCDF) method is a sophisticated ab-initio program for the evaluation of configuration mixing in the relativistic sense (same nl, but different j 's).

We can expect that the same procedure, using virtual orbitals,

will be successful in the relativistic case of configuration mixing evaluations with different n . In order to achieve convergence in the MCHF method one needs a reasonable initial approximation for the relativistic virtual orbital which will be used as input in Desclaux's code.

The method for the obtention of the virtual orbital is presented in sec. 2.

The virtual orbital was obtained by using the principal configuration orbitals taken from Desclaux's code as frozen orbitals.

The application of the method towards the evaluation of the hyperfine structure in the calcium atom uses the effective operator and the pure relativistic operator in the barium atom is shown in sec. 4.

2. THE METHOD

The virtual orbital radial functions are expanded as a discrete basis of analytical functions⁹. The determination of these functions is not trivial since in Dirac's representation the variational methods can collapse in negative-energy eigenvalues¹³. Therefore we shall choose a basis set which removes these negative eigenvalues.

Drake and Goldman⁹ used the discrete basis-set method in order to solve the Dirac equation by a variational method. They calculated electric dipole oscillator strengths for one-electron system and have shown that this method is capable of separating the energies related to positive - continuum and negative - continuum. In order to determine the virtual orbital we use here the same idea by imposing that the other (core) wave-functions are known and frozen.

The relativistic wave-function representation for one electron is, in general, given by

$$|\phi\rangle = \begin{pmatrix} \frac{G(r)}{r} | \frac{1}{2} \ell jm \rangle \\ i \frac{F(r)}{r} | \frac{1}{2} \bar{\ell} jm \rangle \end{pmatrix} \quad (1)$$

where $\bar{\ell} = 2j - \ell$, and $G(r)$ and $F(r)$ are real radial functions (large and small components respectively).

For convenience, we define the large and small radial functions

$g(r)$ and $f(r)$, both real and belonging to L^2 , so that the real two-component spinor

$$\phi(r) = \begin{pmatrix} g(r) \\ f(r) \end{pmatrix} \quad (2)$$

satisfies the radial Dirac equation

$$H_r \phi(r) = \varepsilon \phi(r) \quad (3)$$

$$H_r = i\alpha\sigma_y \frac{d}{dr} + \alpha\sigma_x \frac{\kappa}{r} - c^2 \sigma_z V(r) \quad (\text{in a.u.})$$

The σ 's are the Pauli spin matrices, and κ is the Dirac quantum number

$$\kappa = (-1)^{j+l+\frac{1}{2}} (j+\frac{1}{2}) \quad (4)$$

The trial functions $\psi(r)$ can be written as

$$\phi(r) = \sum_n h_n(r) \left[a_n \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b_n \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \quad (5)$$

where a 's and b 's are variational parameters and $h_n(r)$ is the orthonormal set over which the trial functions are expanded. We have used $h_n(r)$ functions: the Slater-type basis

$$h_n(r) = \left[\frac{2\lambda}{\Gamma(2(\gamma+n)-1)} \right]^{1/2} r^{\gamma+n-1} e^{-\lambda r} \quad \lambda > 0 \quad (6a)$$

and the generalized Laguerre-type basis

$$h_n(\gamma) = \left[\frac{(n-1)! 2\lambda}{\Gamma(2\gamma+n)} \right]^{1/2} (2\lambda r)^\gamma e^{-\lambda r} L_{n-1}^{2\gamma}(2\lambda r) \quad \lambda > 0 \quad (6b)$$

with

$$\gamma = \left[\kappa^2 - (z/c)^2 \right]^{1/2} .$$

$L_m(x)$ are generalized Laguerre polynomials, A is a nonlinear parameter

which will be adjusted in order to minimize the energy.

After orthonormalization relative to core functions $\phi(x)$ can be written as

$$\phi(x) = \sum_i \begin{pmatrix} G_i \\ F_i \end{pmatrix} \quad (7)$$

with $G_i = a_i g_i$ and $F_i = b_i f_i$.

The variational method plays a prominent role in the construction of approximate eigenvalues and eigenfunctions in nonrelativistic quantum mechanics. In general it cannot be extended to the Dirac Hamiltonian because it is expected to yield an unlimited collapse to negative energy eigenvalues. Drake and Goldman⁹ have proved a generalized Hyllerraas-Undheim theorem¹⁰ for the special case of the Coulomb potential ($V(r) = 1/r$). They gave a rigorous proof for the particular case of just one term in equation (5).

The stability of the solution for the Dirac-Fock equation was discussed by Desclaux *et al*^{8,11} and Kim¹², and the collapse for the negative energy state was discussed by Datta¹³.

Recently Gran¹⁴ has analysed the eigenvalues with division into N positive-energy and N negative-energy choices for a N basis set, and the appearance of a sort of Hyllerraas-Undheim theorem for the positive eigenvalues E_j^+ .

With the condition

$$\int_0^\infty |f(r)^2 + g(r)^2| dr = 1$$

we have

$$\int_0^\infty \phi_i H_r \phi_j dr = \epsilon_i \delta_{ij} \quad (8)$$

For two bases in hydrogenlike atoms the left-hand side of eq. (8) gives

$$\underbrace{\begin{pmatrix} a_1 & b_1 & a_2 & b_2 \end{pmatrix}} = \begin{pmatrix} \frac{1}{\alpha} A_{11} - \alpha B_{11} & C_{11} + kD_{11} & \frac{1}{\alpha} A_{12} - \alpha B_{12} & C_{12} + D_{12} \\ -\frac{1}{\alpha} A'_{11} - \alpha B'_{11} & C'_{12} + kD_{12} & -A'_{12} - \alpha D_{12} & \\ & \frac{1}{\alpha} A_{22} - \alpha B_{22} & C_{22} + kD_{22} & \\ & & -\frac{1}{\alpha} A'_{22} - \alpha B'_{22} & \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \\ a_2 \\ b_2 \end{pmatrix} \quad (9)$$

with

$$A_{ij} = \int g_i g_j dr$$

$$A'_{ij} = \int f_i f_j dr$$

$$B_{ij} = \int g_i v(r) g_j dr$$

$$B'_{ij} = \int f_i v(r) f_j dr$$

$$C_{ij} = \int g_i \frac{d}{dr} f_j dr$$

$$C'_{ij} = \int f_i \frac{d}{dr} g_j dr$$

and

$$D_{ij} = \int f_i v(r) g_j dr$$

In the present paper we are not interested in hydrogen-like atoms, but in a determination of the excited state virtual orbital for complex atoms. Therefore we have to include the Coulomb term $1/r_{ij}$ (in eq. (4)) between the basis functions $\left(\frac{G_i}{F_i}\right)$ and the core orbital $\left(\frac{g_a}{f_a}\right)$.

The contribution of the Coulomb terms is given as a function of the Slater integrals. These are defined by

$$F^k(a, b) = R^k(a, a, b, b) \text{ and } G^k(a, b) = R^k(a, b, a, b) \quad (10a)$$

with

$$R^k(a, b, c, d) = \int_0^\infty \int_0^\infty (G_a G_b + F_a F_b) \frac{r^k}{r^{k+1}} (G_c G_d + F_c F_d) dr_1 dr_2$$

where F^k and G^k are respectively the direct and the exchange interaction between electron pairs. With the Slater integrals between the basis functions $\begin{pmatrix} G \\ F \end{pmatrix}_i$ and the core orbitals $\begin{pmatrix} G \\ F \end{pmatrix}_0$ we can put eq. (10a) in the form

$$F^k(i, 0) = a_i^2 AA_{i0} + b_i^2 AA'_{i0} \tag{10b}$$

and

$$G^k(i, 0) = \alpha^2 BB_{i0} + \alpha_i b_i C_{i0} + b_i^2 BB'_{i0}$$

with

$$\begin{aligned} AA_{i0} &= \int_0^\infty \int_0^\infty g_i^2 (g_0^2 + f_0^2) \frac{1}{r_{i0}} dr_1 dr_2 \\ AA'_{i0} &= \int_0^\infty \int_0^\infty f_i^2 (g_0^2 + f_0^2) \frac{1}{r_{i0}} dr_1 dr_2 \\ BB_{i0} &= \int_0^\infty \int_0^\infty g_i^2 g_0^2 \frac{1}{r_{i0}} dr_1 dr_2 \\ BB'_{i0} &= \int_0^\infty \int_0^\infty f_i f_0 \frac{1}{r_{i0}} dr_1 dr_2 \\ CC_{i0} &= \int_0^\infty \int_0^\infty g_0 g_i f_0 f_i \frac{1}{r_{i0}} dr_1 dr_2 \end{aligned} \tag{10c}$$

for two bases

$$\begin{pmatrix} a_1 & b_1 & a_2 & b_2 \end{pmatrix} \begin{pmatrix} AA_{10} + BB_{10} & CC_{10} & 0 & 0 \\ & AA'_{10} + BB'_{10} & 0 & 0 \\ & & AA_{10} + BB_{10} & CC_{20} \\ & & & AA'_{20} + BB'_{20} \end{pmatrix} \begin{pmatrix} a_1 \\ b_1 \\ a_2 \\ b_2 \end{pmatrix} \quad (11)$$

Equation (3) is an expression for hydrogenlike atoms, but (9) and (11) give the new equation

$$\int_0^\infty \phi_i H' \phi_j = \epsilon_i \delta_{ij} \quad (12)$$

which is the equation for the virtual orbital.

The nonlinear parameter λ is adjusted through a numerical optimization method, known as nonlinear simples¹⁵. This method has been used to fit parametric potentials in non-relativistic¹⁶ and relativistic¹⁷ central field calculations, and to obtain a non-relativistic virtual orbital¹⁸. We choose to use the Simplex method because the choice of initial value is not essential in this case.

Our correlated orbital output is not much different from the one obtained with Desclaux's code, but the ratio between large and small components in the $r \rightarrow 0$ limit obtained by us is not satisfactory. Due to the energy, the functions to be optimized have low sensibility on $G(r)$ and $F(r)$ near the origin. On the other hand, energy depends mainly on the large component $G(r)$. If we want a better ratio, we have to impose

$$\frac{G(0)}{F(0)} = \frac{p_0}{q_0} = \frac{z}{c(\gamma + \alpha)}$$

which comes from the series expansions

$$G(r) = p_0 r^\gamma (1 + p_1 r + \dots)$$

and

$$F(r) = q_0 r^Y (1 + q_1 r + \dots)$$

3. RELATIVISTIC HYPERFINE STRUCTURE

It is possible to calculate the relativistic effect in hyperfine structure in two ways:

- a) using the completely relativistic operator
- b) using the effective operator

The hamiltonian for the completely relativistic magnetic dipole interaction between the nuclear moment $\vec{\mu}_N$ and the electron is

$$H_m^R = e \vec{\alpha} \cdot \vec{A}(r) \tag{13}$$

where

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$$

σ are the Pauli matrices and

$$\begin{aligned} \vec{A}(r) &= \vec{\mu}_N \times \vec{r}/r^3 \\ \vec{\mu}_N &= \mu_N \vec{I}/I \end{aligned}$$

We can put H_m^R in the following way

$$H_m^R = i \sqrt{2} e \mu_N \frac{\beta_N}{I} \frac{1}{r^2} \{ \alpha^{(1)} C^{(1)} \alpha^{(1)} \} \cdot I^{(1)} \tag{14}$$

where μ_N is the magnetic nuclear moment in nuclear magnetons, I is the nuclear spin, β_N is the nuclear Born magneton, and e is the electron charge. The reduced matrix element of H_m^R is

$$\begin{aligned}
 \langle n'l'j' || H_m^R || nlj \rangle &= e \mu_N \frac{\beta_N}{I} (-1)^l \left[2(2j+1)(2j'+1) \right]^{1/2} \\
 &\times \begin{pmatrix} j' & 1 & j \\ \frac{1}{2} & -1 & \frac{1}{2} \end{pmatrix} \left[\int_0^\infty \frac{F' G}{r^2} dr + \int_0^\infty \frac{FG'}{r^2} dr \right]
 \end{aligned}
 \tag{15}$$

The introduction of the effective operator formalism by Sanders and Beck¹⁹ in the calculation of hyperfine structure made possible (at that time), not only relativistic evaluations of n-electron spectra, but also comparison between calculated and experimental values of energy levels, which are generally in LS-coupling.

The effective operator involving non-relativistic states $| >$ will have the same matrix elements for H_m^R in the relativistic state $| >$.

$$\langle nlj || T_{\text{eff}}^{(1)} || n'l'j' \rangle = nlj || H_m^R || n'l'j' \rangle$$

where

$$T_{\text{eff}}^{(1)} = \sum_{nl'n'l'} A_{nk}^{(1)}(nl, n'l') \omega^{(kK)^1}(nl, n'l')$$

$\omega^{(kK)^1}$ are double tensor operators of rank one defined by the reduced matrix element²⁰

$$\begin{aligned}
 \langle n_a l_a || \omega^{kK}(nl, n'l') || n_b l_b \rangle &= \\
 &= \left[(2K+1)(2k+1) \right]^{1/2} \delta(n_a l_a, nl) \delta(n_b l_b, n'l')
 \end{aligned}
 \tag{17}$$

The coefficient A_{kK} is given by

$$\begin{aligned}
 A_{kK}^{(1)}(n'l', nl) &= \sum_{ij} \left[(2j+1)(2j'+1)(2k+1)(2K+1) \right]^{1/2} \frac{1}{\sqrt{3}} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & k \\ l & l' & K \\ j & j' & 1 \end{pmatrix} \\
 &\times (nlj || r^{-2} \{ \alpha^{(1)} c^{(1)} \}^{(1)} || n'l'j' \rangle
 \end{aligned}
 \tag{18}$$

In general the configuration mixing is negligible. The diagonal terms are

$$\langle T_j^{(1)} \rangle = \sum_{n\ell} \left[\alpha_{n\ell}^{10} w_{n\ell}^{(10)1} + \alpha_{n\ell}^{01} w_{n\ell}^{(01)1} + \alpha_{n\ell}^{12} w_{n\ell}^{(12)1} \right]$$

We can write $\langle T_j^{(1)} \rangle$ in the non relativistic form

$$\langle T_j^{(1)} \rangle = \frac{e\mu_0}{4\pi} \beta_N \frac{\mu_N}{I} \sum_{n\ell} \left[\ell^{(1)} \langle r_{n\ell}^{-3} \rangle_{01} - \sqrt{10} (s^{(1)} \cdot C^{(1)}) \langle r_{n\ell}^{-3} \rangle_{12} + s^{(1)} \langle r_{n\ell}^{-3} \rangle_{10} \right] \quad (19)$$

where the quantity $\langle r_{n\ell}^{-3} \rangle$ can be expanded in a linear combination of integrals $\int_0^\infty G F r^{-2} dr$ ^{19,20}.

4. RESULTS

4.1 - Results for Barium

In the completely relativistic scheme we calculated the magnetic hyperfine structure constant $A(3P_1)$ for the isotope ¹³⁵Ba in five configurations $sp + dp$ for $j = 1$. Let

$$A_j = \frac{(j_1 j_2 J || H_m^R || j_1' j_2' J)}{(j || j || j)} \quad (20)$$

where

$$(j_1 j_2 J || H_m^R || j_1' j_2' J) = \delta_{(j_1, j_2'), (-1)^{j_1+j_2+1} (2J+1) \begin{pmatrix} j_1 & 1 & J \\ j_1 & j_2 & j_2 \end{pmatrix} \langle H_m^R \rangle \quad (21)$$

and

$$\langle H_m^R \rangle = \sum_i \alpha_i^2 (n\ell j || H_m^R || n\ell j) + 2 \sum_{i>j} \alpha_i \alpha_j (n\ell j || H_m^R || n'\ell'j')$$

The reduced matrix elements are given by eq. (15), and α_i 's are the configuration state amplitude functions calculated with Desclaux's code. The wave function is given by

$$\begin{aligned} \psi = & 0.8631 \left| 6s_{\frac{1}{2}} 6p_{\frac{1}{2}} 1 \right\rangle + 0.4671 \left| 6s_{\frac{1}{2}} 6p_{\frac{3}{2}} 1 \right\rangle - 0.1127 \left| 6p_{\frac{1}{2}} 5d_{\frac{3}{2}} 1 \right\rangle \\ & - 0.1563 \left| 6p_{\frac{3}{2}} 5d_{\frac{3}{2}} 1 \right\rangle + 0.01404 \left| 6p_{\frac{3}{2}} 5d_{\frac{5}{2}} 1 \right\rangle \end{aligned} \quad (22)$$

From eqs. (21) and (22) we have for A_{3P_1} , the diagonal contribution 725.56 MHz and the non-diagonal contribution -11.93 MHz, giving the total of 713.65 MHz. The experimental value by zu Putlitz²¹ is $A_{3P_1} = 1090$ MHz. Therefore our result is 66% of the experimental value. If we use only the sp configurations, the wave functions is given by

$$\psi = 0.8344 \left| 6s_{\frac{1}{2}} 6p_{\frac{1}{2}} 1 \right\rangle + 0.5510 \left| 6s_{\frac{1}{2}} p_{\frac{3}{2}} 1 \right\rangle$$

and we obtain $A_{(3P_1)} = 679.19$ MHz, which is 62% of zu Putlitz's value, showing that orbital d mixing is not enough.

In the purely relativistic case, the magnetic hyperfine structure operator does not have several terms, as in the non-relativistic case. To obtain the spin polarization effect, we calculated the spin polarization Hartree-Fock (SPHF) in the non relativistic $6s 6p$ configuration, and we found that spin-polarization increased the magnetic hyperfine structure term α^{10} (Fermi's contact) by 23%.

The jj - LS coupling gives

$$\left| \left| {}^3P \right\rangle \right\rangle = 0.999892 \left| {}^3P_1 \right\rangle - 0.031881 \left| {}^1P_1 \right\rangle$$

Therefore the 3P level is almost pure LS coupling, allowing one to make the non-relativistic calculation. With the spin-polarization we have

$$A_{(3P)} = 1427.25 \left(\frac{1}{4} \alpha_{6s}^{10} + \frac{1}{4} \alpha_{6p}^{10} + \frac{1}{2} \alpha_{6p}^{01} + \frac{1}{2} \alpha_{6p}^{12} \right) \quad (\text{in MHz}) .$$

After the α are evaluated, we have, for $A_{(3P)}$ the value 880.53 MHz, which shows that spin polarization is very important.

4.2 - Results for Calcium

We used the effective operator in the calculation of the electronic parameters a_{nl}^{jv} ($jv = 10, 01, 12$) and b_{nl}^{jv} of the hyperfine structure of the $[4s^2 3p^1 4p^2]$ level in the calcium atom, with five mixing configurations in $4s 4p$ and $3d 4p$ for $j = 1$.

Our results for MCDF, MCHF and for monoconfigurational DF and HF as well as the LS-dependent Hartree-Fock (LSHF) of Olsson and Salomonson²³ are displayed in table 1.

Table 1 - The MCDF values of (r^{-3}) for Ca^3P level (in a.u.).

Method	$\langle r^{-3} \rangle_{10}$	$\langle r^{-3} \rangle_{10}$	$\langle r^{-3} \rangle_{12}$	$\langle r^{-3} \rangle_{02}$
HF	13.07	0.637	0.637	0.637
DF	13.79	0.648	0.669	0.647
MCHF ⁸	12.05	0.912	0.969	1.01
	14.51 ⁺		1.025*	
LSHF ²³	12.49	0.992	1.021	1.142
	15.24		1.072*	
MCDF	12.94	0.950	1.03	0.90
exp ²³	17.5(1)		1.08(4)	

⁺with spin polarization; *with relativistic correction.

5. DISCUSSION

The use of the method described in 1 gives us the virtual $6p_{3/2}^2$, $5d_{3/2}^2$ and $5d_{5/2}^2$ orbitals for Barium and $3d_{3/2}^2$ and $3d_{5/2}^2$ for calcium atoms. Without these orbitals the utilization of Desclaux's code in the multiconfigurational calculus is not possible.

In the calculation of the Hyperfine Structure for Ba we could

verify that five configuration results are better than using two configurations (66% and 62% of the experimental values **respectively**). On the other hand non-relativistic HF in the $6s\ 6p\ ^3P$ configuration gave 81% of the experimental value where 23% is due to the spin polarization (SPHF calculus) in the a_{6s}^{10} term.

Desciaux²² has made the same calculations with spinpolarization (relativistic) and verified that **it is** of the same order of the non-relativistic calculations. This would improve our results, though not significantly. A **possibility** is to include, in addition to the spin polarization, the orbital polarization and the correlation (bi-excitation). But this would be very difficult due to the large number of configurations since relativistic wave functions have, for the same $n\ell$, the orbitals $n\ell \pm \frac{1}{2}$ ($R > 0$).

Observing table 1 we verify that in the determination of the SF electronic constant in Ca we have generally better MCF values than DF values. We can also notice that the multiconfigurational non-relativistic MCF and LSHF values for the Fermi term $\langle r^{-3} \rangle^{10}$ without spin polarization have about the same values as given by MCF. Considering spin polarization, the non-relativistic multiconfigurational calculations are close to the experimental values.

In the orbital term $\langle r^{-3} \rangle^{01}$ we verify that the three multiconfigurational methods give nearly the same values, and the $\langle r^{-2} \rangle^{02}$ value obtained through MCF is just a little smaller than those obtained through MCF and LSHF methods. We can also verify that in the dipole-spin term $\langle r^{-3} \rangle^{12}$ for the non-relativistic calculation, the orbital polarization contribution is not as important as the spin polarization for Fermi term. Therefore, without relativistic corrections, the values obtained through MCF and LSHF methods are just a little smaller than those obtained through MCF. **But**, after relativistic corrections, we obtained through MCF the same MCF result and an LSHF result closer to the experimental value.

6. CONCLUSION

By using a discrete basis set to obtain the relativistic virtual orbital **it becomes possible** to use relativistic multiconfigur-

ational calculations. It is known that relativistic multiconfigurational treatment involves more orbitals than an equivalent non-relativistic treatment. If we increase the number of configurations looking for a better result, the calculation should be more difficult, but probably would converge. As we have noticed, the use of core polarization in non-relativistic calculations is more important than the relativistic effect, even in heavy atoms like barium. This confirms the importance of configuration mixing for alkaline-earths^{4,5,23}. On the other hand we know the small influence of those effects in transition - metals²⁴⁻²⁶. This is a motivation for future calculations considering elements of this family.

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Resumo

Apresentamos um método para obter orbitais virtuais relativísticos, construído a partir de um conjunto de bases discretas. Utilizamos estes orbitais em um cálculo multi-configuracional com cinco configurações $sp+dp$ para $j=1$, na obtenção da constante hiperfina eletrônica: $(r^{-3})^{\mu\nu}$, com $\mu\nu = 10, 01, 12$ e 02 , utilizando operadores efetivos para o nível 3P_1 do cálcio e a constante hiperfina $A(^3P_1)$ do bário.