Smeared Coulomb potential orbitals:

I- Asymptotic expansion

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Abstract

We consider an 1-electron model Hamiltonian, whose potential energy corresponds to the Coulomb potential of an infinite wire with charge Z distributed according to a Gaussian function. The time independent Schrödinger equation for this Hamiltonian is solved perturbationally in the asymptotic limit of small amplitude vibration (Gaussian function width close to zero). We propose to use the naturally polarized functions so-obtained, as orbital basis sets for quantum chemical calculations. In particular, they should be well suited to perform electron-nucleus mean field configuration interaction calculations. Since the free-parameters of the model have the remarkable property to factorize the perturbative corrections to the eigenfunctions, these corrective part in factor can be simply added as additional functions to standard basis sets, leaving it to the molecular orbital calculation to optimize the free parameters within molecular orbital coefficients.

1 Introduction

This paper is dedicated to Prof. Graham Chandler for his 80th birthday. His famous “McLean and Chandler basis sets” have proved extremely useful to the quantum chemistry community. Some twenty years ago, we optimized Gaussian basis sets for molecular fragments together with D. Jayatilaka and G. S. Chandler¹. However, this endeavour was suspended due to technical difficulties raised by electronegative atoms. In the present article, we come back to, perhaps, a more original approach to basis functions, where the latter are not selected on the ground of their technical advantages, as was the case initially for Gaussian-type orbitals (GTO)², but because they are eigenfunctions of a model Hamiltonian and therefore have some physical relevance. It is hoped that this property can be taken advantage of in basis set truncation.

The model Hamiltonian we will consider, is a generalization of the hydrogenoid atom Coulomb Hamiltonian. So, our new orbitals will be part of the exponential-type orbitals (ETO)³ family, like the hydrogenoid atom eigenfunctions, which constitute an asymptotic limit. Slater-type orbitals (STO)^{4,5} is another type of ETO related to hydrogenoid orbitals (HO): they can be seen as “uncontracted” HO, that is to say, as HO with the Laguerre polynomial prefactor replaced by a simple monomial one. In contrast to GTO, the difficulty of computing multicenter integrals with STO has led to the introduction of more ETO family members such as Bessel-type orbitals (BTO)⁶ or Coulomb-Sturmian orbitals (CSO)⁷. The techniques developed for the latter^{8–10} will be equally relevant for integrals involving our deformed hydrogenoid orbitals (DHO).

It is our take that DHO will be particularly useful for the recently developed electron-nucleus mean field configuration interaction (EN-MFCI) method¹¹. The EN-MFCI method affords one to obtain in a single calculation, the electronic and vibrational energy levels of a molecule, without making the “Born-Oppenheimer” (BO) approximation^{11,12}. In contrast,

the traditional methods of Quantum Chemistry are set in the frame of this approximation. They describe electronic clouds of fixed nuclear configurations and make use of orbital basis sets centered on nuclear positions. The latter basis sets are not appropriate for EN-MFCI calculations and their discrepancies have been bypassed so far, only by adding off-centered orbitals. However, the addition of such functions introduces linear dependencies within the orbital set and spans virtual molecular orbitals of little relevance for the description of low energy wave functions of the molecule. So, it appears important to develop new orbital basis functions for the EN-MFCI method, able to describe the smeared electronic cloud of oscillating nuclei in a molecular system.

This article is the first part of a series aiming at deriving appropriate basis functions for EN-MFCI calculations. We propose to use the eigenfunctions of a one-electron model Hamiltonian corresponding to a Coulomb potential convoluted with a Gaussian function. The latter can be seen as a ground state vibrational eigenfunction for the nuclear internal motion in the harmonic approximation. In the next section, we show how such Hamiltonian can be expanded asymptotically near the infinitely small Gaussian width limit, where the hydrogenoid atom eigenfunctions are retrieved. Then, in section 3, we solve the eigenproblem for the first order corrected potential by means of the Rayleigh-Schrödinger perturbation theory. We tabulate the first order corrected eigenfunctions and associated eigenvalues up to $n = 7$. In the last section, we provide details and perspectives on how these eigenfunctions can be employed in multi-electron, quantum chemical calculations. Numerical applications of EN-MFCI making use of these new functions is postponed to part two of this series.

2 Asymptotic expansion of a smeared Coulombic Hamiltonian

Let us consider the one-electron model Hamiltonian: $H = -\frac{\Delta}{2\mu} + V(\vec{r})$, with a potential of the form:

$$V(\vec{r}) = -Z \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} \frac{\exp[-az_0^2]}{\|\vec{r} - \vec{r}_{z_0}\|} dz_0, \quad (1)$$

where, $Z \in \mathbb{N}^*$, $a \in \mathbb{R}_+^*$, $\vec{r} = (x, y, z)$ and $\vec{r}_{z_0} = (0, 0, z_0)$ in Cartesian coordinates. When $\vec{r}$ is expressed in cylindrical coordinates, $\vec{r} = (\rho, \phi, z)$, the potential depends only upon ρ and z ,

$$V(\rho, z) = -Z \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} \frac{\exp[-az_0^2]}{\sqrt{\rho^2 + (z - z_0)^2}} dz_0. \quad (2)$$

This potential corresponds to the Coulomb potential of an infinite wire with charge Z distributed according to a Gaussian function. In the limiting case of a Gaussian function sharply peaking at the origin ($a \rightarrow +\infty$, Dirac distribution limit), the system will tends towards a point-charge Z concentrated at the origin and the hydrogenoid atom eigenfunctions will be recovered.

However, by taking a Gaussian width parameter of the order of magnitude of a nucleus vibration amplitude, we will get basis functions corresponding to a Coulomb potential convoluted by a nuclear, vibrational, harmonic motion, that we may think particularly appropriate for EN-MFCI calculations.

Unfortunately, the Schrödinger equation for this potential is hard to solve because the whole z -axis is singular. So, we will restrict ourselves to the $a \rightarrow \infty$ asymptotic limit, and expand

the potential $V(\rho, z)$ as

$$\begin{aligned}
V(\rho, z) &= \frac{-Z\sqrt{a}}{\pi} \int_0^{+\infty} \frac{d\lambda}{\sqrt{\lambda}} \int_{-\infty}^{+\infty} dz_0 \exp[-az_0^2 - \lambda(\rho^2 + (z - z_0)^2)] \\
&= -Z\sqrt{\frac{a}{\pi}} \int_0^{+\infty} \frac{d\lambda}{\sqrt{\lambda(a+\lambda)}} \exp[-\lambda(\rho^2 + z^2)] \exp[\frac{\lambda^2}{a+\lambda} z^2] \\
&= \frac{-Z}{\sqrt{\pi}} \int_0^{+\infty} d\lambda \left(\frac{1}{\sqrt{\lambda}} + \frac{-\frac{\lambda}{2} + z^2 \lambda^2}{\sqrt{\lambda} a} + \frac{\lambda^{3/2}(3 - 12z^2\lambda + 4z^4\lambda^2)}{8a^2} + \frac{\lambda^{5/2}(-15 + 90z^2\lambda - 60z^4\lambda^2 + 8z^6\lambda^3)}{48a^3} + o\left(\frac{1}{a}\right)^{\frac{7}{2}} \right) \exp[-\lambda(\rho^2 + z^2)]
\end{aligned} \tag{3}$$

Swaping the limits and setting $r = \sqrt{\rho^2 + z^2}$, $\rho = r \times \sin(\theta)$, $z = r \times \cos(\theta)$, with $\theta \in [0, \pi]$, the potential becomes

$$V(r, \theta) = -\frac{Z}{r} + \frac{(1 - 3\cos(\theta)^2)Z}{4r^3a} - \frac{3((3 - 30\cos(\theta)^2 + 35\cos(\theta)^4)Z)}{32r^5a^2} + \frac{15(5 - 105\cos(\theta)^2 + 315\cos(\theta)^4 - 231\cos(\theta)^6)Z}{128r^7a^3} + O\left[\frac{1}{a}\right]^4, \tag{4}$$

where we recognize the hydrogenoid atom potential in the zeroth-order term,

$$V^{(0)}(r, \theta) = -\frac{Z}{r}. \tag{5}$$

Now, at any order, the singularity is located at the single point $r = 0$. In the following, we will only consider the $V(r, \theta)$ potential truncated at first order,

$$V_1(r, \theta) := -\frac{Z}{r} + \frac{(1 - 3\cos(\theta)^2)Z}{4r^3a}. \tag{6}$$

Since this potential is not bounded from below, we will not attempt to solve the eigenproblem exactly. Instead, we apply Rayleigh-Schrödinger perturbation theory, to obtain the first order corrections to the hydrogenoid atom eigenstates.

3 Perturbationally corrected eigenstates

So, we consider the following Hamiltonian in spherical coordinates and atomic units

$$H = \frac{-1}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin(\theta)^2} \frac{\partial^2}{\partial \phi^2} \right) + V_1(r, \theta), \quad (7)$$

defined on the Hilbert space of square integrable functions whose scalar product is expressed as,

$$\langle \psi_1 | \psi_2 \rangle := \int_0^{+\infty} r^2 dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \psi_1^*(r, \theta, \phi) \psi_2(r, \theta, \phi). \quad (8)$$

A Galerkin-type approach similar to the one proposed in ¹³, with spherical harmonics in place of Chebychev basis functions could be considered to solve its eigenvalue problem. However, it is more practical to approach the eigenstates perturbationally, starting from the well-known solutions of time-independent Schrödinger equation for the hydrogenoid atom,

$$\psi_{n,l,m}^{(0)}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi) \quad (9)$$

with

$$R_{n,l}(r) = \left(\frac{2\mu Z}{n} \right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]}} \exp\left(-\frac{\mu Z r}{n}\right) \left(\frac{2\mu Z r}{n} \right)^l L_{n-l-1}^{2l+1}\left(\frac{2\mu Z r}{n}\right), \quad (10)$$

where $L_{n-l-1}^{2l+1}(x)$ denotes the generalized Laguerre polynomials, and $Y_{l,m}(\theta, \phi)$ the spherical harmonics. We note that the perturbation operator,

$$V^{(1)}(r, \theta) := \left(\frac{1}{a} \right) \frac{(1 - 3\cos(\theta)^2) Z}{4r^3}. \quad (11)$$

is proportional to $Y_{2,0}(\theta, \phi)$,

$$V^{(1)}(r, \theta) = \sqrt{\frac{\pi}{5}} \left(\frac{-Z}{a} \right) \frac{Y_{2,0}(\theta, \phi)}{r^3}. \quad (12)$$

Given the following integral formula

$$\int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi Y_{l_1, m_1}(\theta, \phi) Y_{l_2, m_2}(\theta, \phi) Y_{l_3, m_3}(\theta, \phi) = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \quad (13)$$

and the well-known relation for the conjugate of a spherical harmonic:

$$Y_{l,m}^*(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi), \quad (14)$$

we deduce that, for a given (n, l, m) -triplet of quantum numbers, the state $\psi_{n,l,m}^{(0)}$ can only be coupled at first order to states $\psi_{n',l',m'}^{(0)}$'s such that (i) $l' \geq |m|$, (ii) for $l' \in \{|l-2|, \dots, l+2\}$, the 3-j symbol $\begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix}$ is non zero, and, (iii) $n' > l'$. The allowed quantum number values are summed up in Tab.1.

Table 1: List of hydrogenoid eigenstates coupled by the perturbation operator of Eq.(12) to a given hydrogenoid eigenstate (in terms of their associated quantum numbers).

Zero-order states	states possibly coupled by first-order perturbation
$n > 0, l = 0, m = 0$	$(n' > 2, l' = 2, m' = 0)$
$n > 1, l = 1, m \in \{-1, 0, 1\}$	$(n' > 1, l' = 1, m' = m); (n' > 3, l' = 3, m' = m)$
$n > l \geq 2, m \in \{-l, -l+1, l-1, l\}$	$(n' > l, l' = l, m' = m); (n' > l+2, l' = l+2, m' = m)$
$n > l \geq 2, m \in \{-l+2, \dots, l-2\}$	$(n' > l-2, l' = l-2, m' = m); (n' > l, l' = l, m' = m); (n' > l+2, l' = l+2, m' = m)$

A priori, the perturbation operator needs to be diagonalized first in each degenerate n -subspace. The first order correction to the unperturbed energies, (that is the energies of the hydrogenoid atom, $E_{n,l,m}^{(0)} = -\frac{\mu Z^2}{2n^2}$ in hartree), are the eigenvalues of the matrix,

$$(\langle \psi_{n,l,m}^{(0)} | V^{(1)} | \psi_{n',l',m'}^{(0)} \rangle)_{(l,m),(l',m')} = (\delta_{m,m'} \langle \psi_{n,l,m}^{(0)} | V^{(1)} | \psi_{n,l,m}^{(0)} \rangle)_{(l,m),(l',m')}. \quad (15)$$

However, this matrix is already diagonal: For $m = m'$ and $l \neq l'$ a non-zero integration on angular variables implies $l = l' \pm 2$, as we have seen. Suppose without loss of generality, that $l = l' + 2$, the problem being symmetrical in l and l' . The generalized Laguerre polynomial $L_{n-l-1}^{2l+1} \left(\frac{2\mu Zr}{n} \right) = L_{n-l'-3}^{2l'+5} \left(\frac{2\mu Zr}{n} \right)$ can be expanded as a linear combination of generalized Laguerre polynomial $L_i^{2l'+1} \left(\frac{2\mu Zr}{n} \right)$ with $i \leq n - l' - 3$. All these polynomials are orthogonal to $L_{n-l'-1}^{2l'+1} \left(\frac{2\mu Zr}{n} \right)$ for the measure $\left(\frac{2\mu Zr}{n} \right)^{(2l'+1)} \exp \left(-\frac{2\mu Zr}{n} \right)$ which is proportional

to the factor appearing in front of the generalized Laguerre polynomials in the radial integral $\langle R_{n,l} | \frac{1}{r^3} | R_{n,l'} \rangle$.

So, for $l = 0$, there is no first order correction,

$$E_{n,0,0} = -\frac{\mu Z^2}{2n^2}, \quad (16)$$

and for $l > 0$, the correction is,

$$\begin{aligned} E_{n,l,m} &= E_{n,l,m}^{(0)} - \sqrt{\frac{\pi}{5}} \left(\frac{Z}{a} \right) \langle \psi_{n,l,m}^{(0)} | \frac{Y_{2,0}(\theta, \phi)}{r^3} | \psi_{n,l,m}^{(0)} \rangle \\ &= -\frac{\mu Z^2}{2n^2} - \sqrt{\frac{\pi}{5}} \left(\frac{Z}{a} \right) \int_0^{+\infty} \frac{R_{n,l}^2(r)}{r} dr \times (-1)^m \left(l + \frac{1}{2} \right) \sqrt{\frac{5}{\pi}} \begin{pmatrix} l & l & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 2 \\ -m & m & 0 \end{pmatrix} \\ &= -\frac{\mu Z^2}{2n^2} - \left(\frac{Z}{a} \right) \times (-1)^m \left(l + \frac{1}{2} \right) \begin{pmatrix} l & l & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & 2 \\ -m & m & 0 \end{pmatrix} \int_0^{+\infty} \frac{R_{n,l}^2(r)}{r} dr. \end{aligned} \quad (17)$$

As expected, the spherical symmetry is broken: an $(l, |m|)$ -dependency is introduced in the perturbed eigenvalues. In Tab.2, we provide the first order eigenvalues, which can be useful for basis set truncation purposes. We note that, at first order, degeneracy is not completely lifted, as for example, $E_{4,0,0} = E_{4,3,\pm 2}$. If we factorize by the zero order energy, we see that the relative, first order corrections are all proportional to $\frac{\mu^2 Z^2}{a}$.

Table 2: First-order corrected energies (up to $n=4$). For every pairs, (n, l) , the sum over $m \in \{-l, -l+1, \dots, l-1, l\}$ of the first order corrections is zero. The spacing between the energies does not follow any scale, only the order between the levels is respected.

	$l = 0$	$l = 1$	$l = 2$	$l = 3$
$n = 4$	$E_{4,0,0} = -\frac{\mu Z^2}{32}$	$E_{4,1,\pm 1} = -\frac{\mu Z^2}{32} + \frac{\mu^3 Z^4}{1920a}$	$E_{4,2,\pm 2} = -\frac{\mu Z^2}{32} + \frac{\mu^3 Z^4}{6760a}$	$E_{4,3,\pm 3} = -\frac{\mu Z^2}{32} + \frac{\mu^3 Z^4}{16128a}$ $E_{4,3,\pm 2} = -\frac{\mu Z^2}{32}$ $E_{4,3,\pm 1} = -\frac{\mu Z^2}{32} - \frac{\mu^3 Z^4}{26880a}$ $E_{4,3,0} = -\frac{\mu Z^2}{32} - \frac{\mu^3 Z^4}{20160a}$
		$E_{4,1,0} = -\frac{\mu Z^2}{32} - \frac{\mu^3 Z^4}{960a}$	$E_{4,2,\pm 1} = -\frac{\mu Z^2}{32} - \frac{\mu^3 Z^4}{13440a}$ $E_{4,2,0} = -\frac{\mu Z^2}{32} - \frac{\mu^3 Z^4}{6760a}$	
$n = 3$	$E_{3,0,0} = -\frac{\mu Z^2}{18}$	$E_{3,1,\pm 1} = -\frac{\mu Z^2}{18} + \frac{\mu^3 Z^4}{810a}$	$E_{3,2,\pm 2} = -\frac{\mu Z^2}{18} + \frac{\mu^3 Z^4}{2835a}$ $E_{3,2,\pm 1} = -\frac{\mu Z^2}{18} - \frac{\mu^3 Z^4}{5670a}$ $E_{3,2,0} = -\frac{\mu Z^2}{18} - \frac{\mu^3 Z^4}{2835a}$	
		$E_{3,1,0} = -\frac{\mu Z^2}{18} - \frac{\mu^3 Z^4}{405a}$		
$n = 2$	$E_{2,0,0} = -\frac{\mu Z^2}{8}$	$E_{2,1,\pm 1} = -\frac{\mu Z^2}{8} + \frac{\mu^3 Z^4}{240a}$	$E_{2,1,0} = -\frac{\mu Z^2}{8} - \frac{\mu^3 Z^4}{120a}$	
$n = 1$	$E_{1,0,0} = -\frac{\mu Z^2}{2}$			

A similar observation can be made for the first order corrected eigenfunctions,

$$\begin{aligned}
\psi_{n,l,m} &= \psi_{n,l,m}^{(0)} + \sum_{(n',l') \neq (n,l)} \frac{-\sqrt{\frac{\pi}{5}} \left(\frac{Z}{a}\right) \langle \psi_{n',l',m}^{(0)} | \frac{Y_{2,0}(\theta,\phi)}{r^3} | \psi_{n,l,m}^{(0)} \rangle}{E_{n,l,m}^{(0)} - E_{n',l',m}^{(0)}} \psi_{n',l',m}^{(0)} \\
&= \psi_{n,l,m}^{(0)} + \sum_{(n',l') \neq (n,l)} \frac{-\left(\frac{Z}{a}\right) \int_0^{+\infty} \frac{R_{n',l'}(r)R_{n,l}(r)}{r} dr \times (-1)^m \sqrt{(l'+\frac{1}{2})(l+\frac{1}{2})} \begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & 2 \\ -m & m & 0 \end{pmatrix}}{-\frac{\mu Z^2}{2n^2} + \frac{\mu Z^2}{2n'^2}} \psi_{n',l',m}^{(0)} \\
&= \psi_{n,l,m}^{(0)} + \sum_{(n',l') \neq (n,l)} \frac{\frac{2n'^2 n^2}{a\mu Z(n'^2 - n^2)} (-1)^m \sqrt{(l'+\frac{1}{2})(l+\frac{1}{2})} \begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & 2 \\ -m & m & 0 \end{pmatrix} \int_0^{+\infty} \frac{R_{n',l'}(r)R_{n,l}(r)}{r} dr}{-\frac{\mu Z^2}{2n^2} + \frac{\mu Z^2}{2n'^2}} \psi_{n',l',m}^{(0)},
\end{aligned} \tag{18}$$

the radial integral being proportional to $\mu^3 Z^3$ (because of the $\frac{1}{r^3}$ -term, as it appears when one makes the change of variables $x = 2\mu Zr$), all the coupling coefficients in the expansion are proportional to $\frac{\mu^2 Z^2}{a}$. Here also, the potentially divergent terms in the expansion, due to the degeneracy of the zeroth order eigenvalues for a given n in the denominators, can be excluded since the corresponding numerators cancel out for the same reason that makes the first order matrix, Eq.(15), diagonal.

The first terms in the expansion of the lowest eigenfunctions are given in Tab. 3. Iso-density surfaces of the density functions corresponding to these eigenfunctions are displayed in Figs. 1 to 10. They shows isosurfaces belonging sometimes to different homology groups for different density values, which give an idea of the repartition of the electronic charge as it becomes more and more concentrated. The parameter $c := \mu \times Z$, which controls how diffuse the unperturbed hydrogenoid orbitals are, is set to 1. The parameter $b := \frac{\mu \times Z}{a}$, which tunes the intensity of the distorsion with respect to spherical symmetry, takes two values: $b = 1$ close to the no distorsion case ($b = 0$), and $b = 32$ for which the effect of the perturbed potential becomes clearly apparent. The perturbed 1s orbital, Fig. 1 for example, becomes elongated along the Coulomb potential spreading axis, as one expects. The variations for other orbitals are sometimes less intuitive.

Table 3: First-order corrected wave functions, ordered in increasing energy eigenvalue up to n=3 (in Appendix we provide a more comprehensive table up to n=7, “i-orbitals”).

$n = 1$	$l = 0$	$m = 0$	$\psi_{1,0,0} = \psi_{1,0,0}^{(0)} + \frac{\sqrt{5}}{5a\mu Z} \sum_{n' > 2} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{1,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{1,0,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{\sqrt{6}}{480} \psi_{3,2,0}^{(0)} + \frac{104}{28125} \psi_{4,2,0}^{(0)} + \frac{5\sqrt{14}}{6804} \psi_{5,2,0}^{(0)} + \frac{5744\sqrt{21}}{12353145} \psi_{6,2,0}^{(0)} + \frac{3299\sqrt{21}}{8847360} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 2$	$l = 0$	$m = 0$	$\psi_{2,0,0} = \psi_{2,0,0}^{(0)} + \frac{4\sqrt{5}}{5a\mu Z} \sum_{n' > 2} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{2,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{2,0,0}^{(0)} - \frac{\mu^2 Z^2}{a} \left(\frac{32\sqrt{3}}{9375} \psi_{3,2,0}^{(0)} + \frac{2\sqrt{2}}{1215} \psi_{4,2,0}^{(0)} + \frac{3680\sqrt{7}}{7411887} \psi_{5,2,0}^{(0)} + \frac{29\sqrt{42}}{215040} \psi_{6,2,0}^{(0)} + \frac{63584\sqrt{42}}{645700815} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 2$	$l = 1$	$m = 0$	$\psi_{2,1,0} = \psi_{2,1,0}^{(0)} + \frac{8}{5a\mu Z} \sum_{n' > 2} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{2,1}(r)}{r} dr \psi_{n',1,0}^{(0)} + \frac{12\sqrt{21}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{2,1}(r)}{r} dr \psi_{n',3,0}^{(0)}$ $= \psi_{2,1,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{192}{3125} \psi_{3,1,0}^{(0)} + \frac{56\sqrt{10}}{6075} \psi_{4,1,0}^{(0)} + \frac{8768\sqrt{5}}{1058841} \psi_{5,1,0}^{(0)} + \frac{201\sqrt{35}}{89600} \psi_{6,1,0}^{(0)} + \frac{2926784\sqrt{14}}{1076168025} \psi_{7,1,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{8\sqrt{10}}{14175} \psi_{4,3,0}^{(0)} + \frac{512\sqrt{5}}{823543} \psi_{5,3,0}^{(0)} + \frac{123\sqrt{10}}{358400} \psi_{6,3,0}^{(0)} + \frac{541184\sqrt{3}}{1076168025} \psi_{7,3,0}^{(0)} + \dots \right)$
$n = 2$	$l = 1$	$m = \pm 1$	$\psi_{2,1,\pm 1} = \psi_{2,1,\pm 1}^{(0)} - \frac{4}{5a\mu Z} \sum_{n' > 2} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{2,1}(r)}{r} dr \psi_{n',1,\pm 1}^{(0)}$ $+ \frac{12\sqrt{14}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{2,1}(r)}{r} dr \psi_{n',3,\pm 1}^{(0)}$ $= \psi_{2,1,\pm 1}^{(0)} - \frac{\mu^2 Z^2}{a} \left(\frac{96}{3125} \psi_{3,1,\pm 1}^{(0)} + \frac{28\sqrt{10}}{6075} \psi_{4,1,\pm 1}^{(0)} + \frac{4384\sqrt{5}}{1058841} \psi_{5,1,\pm 1}^{(0)} + \frac{201\sqrt{35}}{179200} \psi_{6,1,\pm 1}^{(0)} + \frac{1463392\sqrt{14}}{1076168025} \psi_{7,1,\pm 1}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{16\sqrt{15}}{42525} \psi_{4,3,\pm 1}^{(0)} + \frac{512\sqrt{30}}{2470629} \psi_{5,3,\pm 1}^{(0)} + \frac{41\sqrt{15}}{179200} \psi_{6,3,\pm 1}^{(0)} + \frac{541184\sqrt{2}}{1076168025} \psi_{7,3,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 0$	$m = 0$	$\psi_{3,0,0} = \psi_{3,0,0}^{(0)} + \frac{27\sqrt{5}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{3,0,0}^{(0)} - \frac{\mu^2 Z^2}{a} \left(\frac{792\sqrt{3}}{588245} \psi_{4,2,0}^{(0)} + \frac{45\sqrt{42}}{229376} \psi_{5,2,0}^{(0)} + \frac{656\sqrt{7}}{2066715} \psi_{6,2,0}^{(0)} + \frac{1809\sqrt{7}}{7812500} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 3$	$l = 1$	$m = 0$	$\psi_{3,1,0} = \psi_{3,1,0}^{(0)} + \frac{18}{5a\mu Z} \sum_{n' > 1} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{3,1}(r)}{r} dr \psi_{n',1,0}^{(0)} + \frac{27\sqrt{21}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{3,1}(r)}{r} dr \psi_{n',3,0}^{(0)}$ $= \psi_{3,1,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{-192}{3125} \psi_{2,1,0}^{(0)} + \frac{60288\sqrt{10}}{2941225} \psi_{4,1,0}^{(0)} + \frac{231\sqrt{5}}{16384} \psi_{5,1,0}^{(0)} + \frac{35648\sqrt{35}}{10333575} \psi_{6,1,0}^{(0)} + \frac{310191\sqrt{14}}{78125000} \psi_{7,1,0}^{(0)} + \dots \right)$ $- \frac{\mu^2 Z^2}{a} \left(\frac{10368\sqrt{10}}{20588575} \psi_{4,3,0}^{(0)} + \frac{81\sqrt{5}}{458752} \psi_{5,3,0}^{(0)} + \frac{128\sqrt{10}}{3444525} \psi_{6,3,0}^{(0)} + \frac{567\sqrt{3}}{39062500} \psi_{7,3,0}^{(0)} + \dots \right)$
$n = 3$	$l = 1$	$m = \pm 1$	$\psi_{3,1,\pm 1} = \psi_{3,1,\pm 1}^{(0)} - \frac{9}{5a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{3,1}(r)}{r} dr \psi_{n',1,\pm 1}^{(0)} + \frac{27\sqrt{14}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{3,1}(r)}{r} dr \psi_{n',3,\pm 1}^{(0)}$ $= \psi_{3,1,\pm 1}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{96}{3125} \psi_{2,1,\pm 1}^{(0)} - \frac{30144\sqrt{10}}{2941225} \psi_{4,1,\pm 1}^{(0)} - \frac{231\sqrt{5}}{32768} \psi_{5,1,\pm 1}^{(0)} - \frac{17824\sqrt{35}}{10333575} \psi_{6,1,\pm 1}^{(0)} - \frac{310191\sqrt{14}}{156250000} \psi_{7,1,\pm 1}^{(0)} + \dots \right)$ $- \frac{\mu^2 Z^2}{a} \left(\frac{6912\sqrt{15}}{20588575} \psi_{4,3,\pm 1}^{(0)} + \frac{27\sqrt{30}}{458752} \psi_{5,3,\pm 1}^{(0)} + \frac{256\sqrt{15}}{10333575} \psi_{6,3,\pm 1}^{(0)} + \frac{567\sqrt{2}}{39062500} \psi_{7,3,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = 0$	$\psi_{3,2,0} = \psi_{3,2,0}^{(0)} + \frac{9\sqrt{5}}{5a\mu Z} \sum_{n' > 0} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',0}(r)R_{3,2}(r)}{r} dr \psi_{n',0,0}^{(0)} + \frac{18}{7a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $+ \frac{54\sqrt{5}}{35a\mu Z} \sum_{n' > 4} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,0}^{(0)}$ $= \psi_{3,2,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{-\sqrt{6}}{480} \psi_{1,0,0}^{(0)} + \frac{32\sqrt{3}}{9375} \psi_{2,0,0}^{(0)} + \frac{128\sqrt{6}}{1764735} \psi_{4,0,0}^{(0)} + \frac{5\sqrt{30}}{196608} \psi_{5,0,0}^{(0)} + \frac{32}{295245} \psi_{6,0,0}^{(0)} + \frac{392\sqrt{42}}{29296875} \psi_{7,0,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{13824\sqrt{6}}{4117715} \psi_{4,2,0}^{(0)} + \frac{675\sqrt{21}}{802816} \psi_{5,2,0}^{(0)} + \frac{9472\sqrt{14}}{14467005} \psi_{6,2,0}^{(0)} + \frac{7371\sqrt{14}}{15625000} \psi_{7,2,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{135\sqrt{105}}{1605632} \psi_{5,4,0}^{(0)} + \frac{512\sqrt{42}}{4822335} \psi_{6,4,0}^{(0)} + \frac{7749\sqrt{231}}{214843750} \psi_{7,4,0}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = \pm 1$	$\psi_{3,2,\pm 1} = \psi_{3,2,\pm 1}^{(0)} + \frac{9}{7a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,\pm 1}^{(0)} + \frac{9\sqrt{6}}{7a\mu Z} \sum_{n' > 4} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,\pm 1}^{(0)}$ $= \psi_{3,2,\pm 1}^{(0)} + \frac{\mu^2 Z^2}{a} \left(\frac{6912\sqrt{6}}{4117715} \psi_{4,2,\pm 1}^{(0)} + \frac{675\sqrt{21}}{1605632} \psi_{5,2,\pm 1}^{(0)} + \frac{4736\sqrt{14}}{14467005} \psi_{6,2,\pm 1}^{(0)} + \frac{7371\sqrt{14}}{31250000} \psi_{7,2,\pm 1}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{675\sqrt{14}}{3211264} \psi_{5,4,\pm 1}^{(0)} + \frac{512\sqrt{35}}{4822335} \psi_{6,4,\pm 1}^{(0)} + \frac{7749\sqrt{770}}{429687500} \psi_{7,4,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = \pm 2$	$\psi_{3,2,\pm 2} = \psi_{3,2,\pm 2}^{(0)} - \frac{18\sqrt{5}}{35a\mu Z} \sum_{n' > 3} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,\pm 2}^{(0)} + \frac{9\sqrt{3}}{7a\mu Z} \sum_{n' > 4} \frac{1}{1 - \frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,\pm 2}^{(0)}$ $= \psi_{3,2,\pm 2}^{(0)} - \frac{\mu^2 Z^2}{a} \left(\frac{13824\sqrt{6}}{4117715} \psi_{4,2,\pm 2}^{(0)} + \frac{675\sqrt{21}}{802816} \psi_{5,2,\pm 2}^{(0)} + \frac{9472\sqrt{14}}{14467005} \psi_{6,2,\pm 2}^{(0)} + \frac{7371\sqrt{14}}{15625000} \psi_{7,2,\pm 2}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left(\frac{675\sqrt{7}}{3211264} \psi_{5,4,\pm 2}^{(0)} + \frac{256\sqrt{70}}{4822335} \psi_{6,4,\pm 2}^{(0)} + \frac{7749\sqrt{385}}{429687500} \psi_{7,4,\pm 2}^{(0)} + \dots \right)$

4 Application to quantum chemical calculations

In the previous section, we have obtained first order perturbative corrections to the eigenfunctions of a smeared Coulomb potential along an arbitrary axis. Such a potential can represent the average potential felt by an electron bounded to a vibrating nucleus of effective charge Z , effective reduced mass μ and effective classical vibrating amplitude equal to $\sqrt{\frac{2n_{vib}+1}{2a}}$ (in harmonic quantum level n_{vib}). Hence, it is hoped that these approximate eigenstates could be appropriate to describe the electron density of the effective electronic Hamiltonians solved in the EN-MFCI method¹¹.

Although the model Hamiltonian depends upon 3 parameters, μ , Z , and a , its first order approximate eigenstates are parametrized by only two independent ones. They can conveniently be chosen as, $c = \mu Z$ and $b = \frac{\mu Z}{a}$. Furthermore, since the product $b \times c$ factorizes the first order perturbative term in the approximate DHOs expansion, Eq.(18), we propose to just add the functions made of these corrective terms to standard basis sets, and leave it to molecular orbital calculations to optimize their linear combination with the other orbitals.

More precisely, instead of using $\psi_{n,l,m}(b, c)$ of Eq.(18) (making explicit the dependency upon the free parameters), we propose to use

$$\frac{\psi_{n,l,m}^{(1)}(c)}{b \cdot c} = (-1)^m 16n^2 \sqrt{l + \frac{1}{2}} \sum_{(n',l') \neq (n,l)} \frac{n'^2}{(n'^2 - n^2)} \sqrt{l' + \frac{1}{2}} \begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & 2 \\ -m & m & 0 \end{pmatrix} \int_0^\infty \frac{R_{n',l'}(x) R_{n,l}(x)}{x} dx \psi_{n',l',m}^{(0)}(c), \quad (19)$$

which only depends upon c through the $\psi_{n',l',m}^{(0)}(c)$ functions. Setting $DHO_{n,l,m}^{(1)}(c) = \frac{\psi_{n,l,m}^{(1)}(c)}{b \cdot c}$, its linear combination coefficients in the occupied molecular orbitals, obtained for example in a HF calculation, implicitly determine the corresponding coefficient products, $b \cdot c$, and consequently, if c is given, the free parameters b . For instance, in H_2 , there is only one occupied HF orbital of the form, $\psi_1 = \sum_i u_i \chi_i + \sum_j v_j DHO_j^{(1)}$ where the χ_i 's are standard basis functions, and the $DHO_j^{(1)}$ are various DHOs on different centers and/or different

quantum numbers, indexed by j . The u_i, v_j ’s are scalar coefficients. One can avoid the explicit optimization of the $b_j \cdot c_j$ values for each $DHO_j(c_j)$, and just use the v_j ’s values.

An important issue is to calculate efficiently multicenter integrals involving the χ_i ’s and $DHO_j^{(1)}$ ’s orbitals, the former being usually GTOs and the latter ETOs. We will adopt a strategy similar to that of the SMILES module¹⁴, optionally included in the MOLPRO quantum chemistry package¹⁵ to deal with STOs. That is to say, the $DHO^{(1)}$ ’s will be transformed into an GTO-expansion, as also in Ref.¹⁶. However, different Cartesian prefactors will be mixed in the GTO-expansion of a given DHO. The BDF code^{17–19} has been modified to accept contracted GTO having such mixed Cartesian prefactors. Full computational details will be provided in the second paper of this series²⁰. Note that, a recently proposed, alternative strategy could be considered in the future²¹.

A hyperbolic cosine factor can be associated to ETO to provide a “double zeta” character to a minimal basis set²². This can be considered for DHO, as well. However, it seems more natural within our framework to combine different sets of DHO corresponding to atoms in different ionization states, to obtain multi-zeta basis sets. This last option preserves the desirable property for the DHOs to have associated energy eigenvalues, which can be used for truncation purposes.

Beside their application to the EN-MFCI method, which will be investigated in the next paper of the series, DHOs could also be useful for “clamped nuclei” quantum chemistry calculations, as they can be regarded as naturally “sp-hybridized” (unlike spherical harmonics STO). Actually, one could develop other model Hamiltonian distorted from spherical symmetry in more than one direction and obtain their first order approximate eigenfunctions by following the approach presented in this paper. For example, generalization of our convoluted Coulomb potentials could provide model Hamiltonians leading to naturally sp2- or sp3-hybridized DHOs.

Another possible interest for traditional quantum chemistry to be assessed in the future, is the ability of DHOs to replace advantageously polarization orbital sets, since high angular

momentum atomic primitives are already contracted within DHOs.

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Figure 1: Comparison of hydrogen smeared Coulomb potential 1s orbital squared density levels.

Figure 2: Comparison of hydrogen smeared Coulomb potential 2s orbital squared density levels.

Figure 3: Comparison of hydrogen smeared Coulomb potential $2p_z$ orbital squared density levels.

Figure 4: Comparison of hydrogen smeared Coulomb potential $2p_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

Figure 5: Comparison of hydrogen smeared Coulomb potential 3s orbital squared density levels.

Figure 6: Comparison of hydrogen smeared Coulomb potential $3p_z$ orbital squared density levels.

Figure 7: Comparison of hydrogen smeared Coulomb potential $3p_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

Figure 8: Comparison of hydrogen smeared Coulomb potential $3d_{z^2}$ orbital squared density levels.

Figure 9: Comparison of hydrogen smeared Coulomb potential $3d_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

Figure 10: Comparison of hydrogen smeared Coulomb potential $3d_{\pm 2}$ ($m = \pm 2$) orbital squared density levels.

Appendix: First order corrected eigenstates up to n=7

$n = 1$	$E_1^0 = -\frac{\mu Z^2}{2}$	
$l = 0$	$E_{1,0,0}^1 = 0$	
$n = 2$	$E_2^0 = -\frac{\mu Z^2}{8}$	
$l = 0$	$E_{2,0,0}^1 = 0$	
$l = 1$	$E_{2,1,0}^1 = -\frac{\mu^3 Z^4}{120a}$	$E_{2,1,\pm 1}^1 = \frac{\mu^3 Z^4}{240a}$
$n = 3$	$E_3^0 = -\frac{\mu Z^2}{18}$	
$l = 0$	$E_{3,0,0}^1 = 0$	
$l = 1$	$E_{3,1,0}^1 = -\frac{\mu^3 Z^4}{405a}$	$E_{3,1,\pm 1}^1 = \frac{\mu^3 Z^4}{810a}$
$l = 2$	$E_{3,2,0}^1 = -\frac{\mu^3 Z^4}{2835a}$	$E_{3,2,\pm 1}^1 = -\frac{\mu^3 Z^4}{5670a}$ $E_{3,2,\pm 2}^1 = \frac{\mu^3 Z^4}{2835a}$
$n = 4$	$E_4^0 = -\frac{\mu Z^2}{32}$	
$l = 0$	$E_{4,0,0}^1 = 0$	
$l = 1$	$E_{4,1,0}^1 = -\frac{\mu^3 Z^4}{960a}$	$E_{4,1,\pm 1}^1 = \frac{\mu^3 Z^4}{1920a}$
$l = 2$	$E_{4,2,0}^1 = -\frac{\mu^3 Z^4}{6720a}$	$E_{4,2,\pm 1}^1 = -\frac{\mu^3 Z^4}{13440a}$ $E_{4,2,\pm 2}^1 = \frac{\mu^3 Z^4}{6720a}$
$l = 3$	$E_{4,3,0}^1 = -\frac{\mu^3 Z^4}{20160a}$	$E_{4,3,\pm 1}^1 = -\frac{\mu^3 Z^4}{26880a}$ $E_{4,3,\pm 2}^1 = 0$ $E_{4,3,\pm 3}^1 = \frac{\mu^3 Z^4}{16128a}$

$n = 5$	$E_5^0 = -\frac{\mu Z^2}{50}$										
$l = 0$	$E_{5,0,0}^1 = 0$										
$l = 1$	$E_{5,1,0}^1 = -\frac{\mu^3 Z^4}{1875a}$	$E_{5,1,\pm 1}^1 = \frac{\mu^3 Z^4}{3750a}$									
$l = 2$	$E_{5,2,0}^1 = -\frac{\mu^3 Z^4}{13125a}$	$E_{5,2,\pm 1}^1 = -\frac{\mu^3 Z^4}{26250a}$	$E_{5,2,\pm 2}^1 = \frac{\mu^3 Z^4}{13125a}$								
$l = 3$	$E_{5,3,0}^1 = -\frac{\mu^3 Z^4}{39375a}$	$E_{5,3,\pm 1}^1 = -\frac{\mu^3 Z^4}{52500a}$	$E_{5,3,\pm 2}^1 = 0$	$E_{5,3,\pm 3}^1 = \frac{\mu^3 Z^4}{31500a}$							
$l = 4$	$E_{5,4,0}^1 = -\frac{\mu^3 Z^4}{86625a}$	$E_{5,4,\pm 1}^1 = -\frac{17\mu^3 Z^4}{1732500a}$	$E_{5,4,\pm 2}^1 = -\frac{2\mu^3 Z^4}{433125a}$	$E_{5,4,\pm 3}^1 = \frac{\mu^3 Z^4}{247500a}$	$E_{5,4,\pm 4}^1 = \frac{\mu^3 Z^4}{61875a}$						
$n = 6$	$E_6^0 = -\frac{\mu Z^2}{72}$										
$l = 0$	$E_{6,0,0}^1 = 0$										
$l = 1$	$E_{6,1,0}^1 = -\frac{\mu^3 Z^4}{3240a}$	$E_{6,1,\pm 1}^1 = \frac{\mu^3 Z^4}{6480a}$									
$l = 2$	$E_{6,2,0}^1 = -\frac{\mu^3 Z^4}{22680a}$	$E_{6,2,\pm 1}^1 = -\frac{\mu^3 Z^4}{45360a}$	$E_{6,2,\pm 2}^1 = \frac{\mu^3 Z^4}{22680a}$								
$l = 3$	$E_{6,3,0}^1 = -\frac{\mu^3 Z^4}{68040a}$	$E_{6,3,\pm 1}^1 = -\frac{\mu^3 Z^4}{90720a}$	$E_{6,3,\pm 2}^1 = 0$	$E_{6,3,\pm 3}^1 = \frac{\mu^3 Z^4}{54432a}$							
$l = 4$	$E_{6,4,0}^1 = -\frac{\mu^3 Z^4}{149688a}$	$E_{6,4,\pm 1}^1 = -\frac{17\mu^3 Z^4}{2993760a}$	$E_{6,4,\pm 2}^1 = -\frac{\mu^3 Z^4}{374220a}$	$E_{6,4,\pm 3}^1 = \frac{\mu^3 Z^4}{427680a}$	$E_{6,4,\pm 4}^1 = \frac{\mu^3 Z^4}{106920a}$						
$l = 5$	$E_{6,5,0}^1 = -\frac{\mu^3 Z^4}{277992a}$	$E_{6,5,\pm 1}^1 = -\frac{\mu^3 Z^4}{308880a}$	$E_{6,5,\pm 2}^1 = -\frac{\mu^3 Z^4}{463320a}$	$E_{6,5,\pm 3}^1 = -\frac{\mu^3 Z^4}{2779920a}$	$E_{6,5,\pm 4}^1 = \frac{\mu^3 Z^4}{463320a}$	$E_{6,5,\pm 5}^1 = \frac{\mu^3 Z^4}{185328a}$					
$n = 7$	$E_7^0 = -\frac{\mu Z^2}{98}$										
$l = 0$	$E_{7,0,0}^1 = 0$										
$l = 1$	$E_{7,1,0}^1 = -\frac{\mu^3 Z^4}{5145a}$	$E_{7,1,\pm 1}^1 = \frac{\mu^3 Z^4}{10290a}$									
$l = 2$	$E_{7,2,0}^1 = -\frac{\mu^3 Z^4}{36015a}$	$E_{7,2,\pm 1}^1 = -\frac{\mu^3 Z^4}{72030a}$	$E_{7,2,\pm 2}^1 = \frac{\mu^3 Z^4}{36015a}$								
$l = 3$	$E_{7,3,0}^1 = -\frac{\mu^3 Z^4}{108045a}$	$E_{7,3,\pm 1}^1 = -\frac{\mu^3 Z^4}{144060a}$	$E_{7,3,\pm 2}^1 = 0$	$E_{7,3,\pm 3}^1 = \frac{\mu^3 Z^4}{86436a}$							
$l = 4$	$E_{7,4,0}^1 = -\frac{\mu^3 Z^4}{237699a}$	$E_{7,4,\pm 1}^1 = -\frac{17\mu^3 Z^4}{4753980a}$	$E_{7,4,\pm 2}^1 = -\frac{2\mu^3 Z^4}{1188495a}$	$E_{7,4,\pm 3}^1 = \frac{\mu^3 Z^4}{679140a}$	$E_{7,4,\pm 4}^1 = \frac{\mu^3 Z^4}{169785a}$						
$l = 5$	$E_{7,5,0}^1 = -\frac{\mu^3 Z^4}{441441a}$	$E_{7,5,\pm 1}^1 = -\frac{\mu^3 Z^4}{490490a}$	$E_{7,5,\pm 2}^1 = -\frac{\mu^3 Z^4}{735735a}$	$E_{7,5,\pm 3}^1 = -\frac{\mu^3 Z^4}{4414410a}$	$E_{7,5,\pm 4}^1 = \frac{\mu^3 Z^4}{735735a}$	$E_{7,5,\pm 5}^1 = \frac{\mu^3 Z^4}{294294a}$					
$l = 6$	$E_{7,6,0}^1 = -\frac{\mu^3 Z^4}{735735a}$	$E_{7,6,\pm 1}^1 = -\frac{\mu^3 Z^4}{792330a}$	$E_{7,6,\pm 2}^1 = -\frac{\mu^3 Z^4}{1030029a}$	$E_{7,6,\pm 3}^1 = -\frac{\mu^3 Z^4}{2060058a}$	$E_{7,6,\pm 4}^1 = \frac{\mu^3 Z^4}{5150145a}$	$E_{7,6,\pm 5}^1 = \frac{\mu^3 Z^4}{936390a}$	$E_{7,6,\pm 6}^1 = \frac{\mu^3 Z^4}{468195a}$				

Table 4: Zero order eigenvalues and first order corrections up to $n=7$

$n = 1$	$\langle 100 320 \rangle = -\frac{\sqrt{6}}{480}$	$\langle 100 420 \rangle = -\frac{104}{28125}$	$\langle 100 520 \rangle = -\frac{5\sqrt{14}}{6804}$	$\langle 100 620 \rangle = -\frac{5744\sqrt{21}}{12353145}$	$\langle 100 720 \rangle = -\frac{3299\sqrt{21}}{8847360}$	
$n = 2$	$\langle 200 320 \rangle = -\frac{32\sqrt{3}}{9375}$	$\langle 200 420 \rangle = -\frac{2\sqrt{2}}{1215}$	$\langle 200 520 \rangle = -\frac{3680\sqrt{7}}{7411887}$	$\langle 200 620 \rangle = -\frac{29\sqrt{42}}{215040}$	$\langle 200 720 \rangle = -\frac{63584\sqrt{42}}{645700815}$	
	$\langle 210 310 \rangle = -\frac{192}{3125}$	$\langle 210 410 \rangle = -\frac{56\sqrt{10}}{6075}$	$\langle 210 510 \rangle = -\frac{8768\sqrt{5}}{1058841}$	$\langle 210 610 \rangle = -\frac{201\sqrt{35}}{89600}$	$\langle 210 710 \rangle = -\frac{2926784\sqrt{14}}{1076168025}$	
		$\langle 210 430 \rangle = -\frac{8\sqrt{10}}{14175}$	$\langle 210 530 \rangle = -\frac{512\sqrt{5}}{823543}$	$\langle 210 630 \rangle = -\frac{123\sqrt{10}}{358400}$	$\langle 210 730 \rangle = -\frac{541184\sqrt{3}}{1076168025}$	
	$\langle 211 311 \rangle = -\frac{96}{3125}$	$\langle 211 411 \rangle = -\frac{28\sqrt{10}}{6075}$	$\langle 211 511 \rangle = -\frac{4384\sqrt{5}}{1058841}$	$\langle 211 611 \rangle = -\frac{201\sqrt{35}}{179200}$	$\langle 211 711 \rangle = -\frac{1463392\sqrt{14}}{1076168025}$	
		$\langle 211 431 \rangle = -\frac{16\sqrt{15}}{42525}$	$\langle 211 531 \rangle = -\frac{512\sqrt{30}}{2470629}$	$\langle 211 631 \rangle = -\frac{41\sqrt{15}}{179200}$	$\langle 211 731 \rangle = -\frac{541184\sqrt{2}}{1076168025}$	
$n = 3$	$\langle 300 420 \rangle = -\frac{792\sqrt{3}}{588245}$	$\langle 300 520 \rangle = -\frac{45\sqrt{42}}{229376}$	$\langle 300 620 \rangle = -\frac{656\sqrt{7}}{2066715}$	$\langle 300 720 \rangle = -\frac{1809\sqrt{7}}{7812500}$		
	$\langle 310 210 \rangle = -\frac{192}{3125}$	$\langle 310 410 \rangle = -\frac{60288\sqrt{10}}{2941225}$	$\langle 310 510 \rangle = -\frac{231\sqrt{5}}{16384}$	$\langle 310 610 \rangle = -\frac{35648\sqrt{35}}{10333575}$	$\langle 310 710 \rangle = -\frac{310191\sqrt{14}}{78125000}$	
		$\langle 310 430 \rangle = -\frac{10368\sqrt{10}}{20588575}$	$\langle 310 530 \rangle = -\frac{81\sqrt{5}}{458752}$	$\langle 310 630 \rangle = -\frac{128\sqrt{10}}{3444525}$	$\langle 310 730 \rangle = -\frac{567\sqrt{3}}{39062500}$	
	$\langle 311 211 \rangle = -\frac{96}{3125}$	$\langle 311 411 \rangle = -\frac{30144\sqrt{10}}{2941225}$	$\langle 311 511 \rangle = -\frac{231\sqrt{5}}{32768}$	$\langle 311 611 \rangle = -\frac{17824\sqrt{35}}{10333575}$	$\langle 311 711 \rangle = -\frac{310191\sqrt{14}}{156250000}$	
		$\langle 311 431 \rangle = -\frac{6912\sqrt{15}}{20588575}$	$\langle 311 531 \rangle = -\frac{27\sqrt{30}}{458752}$	$\langle 311 631 \rangle = -\frac{256\sqrt{15}}{10333575}$	$\langle 311 731 \rangle = -\frac{567\sqrt{2}}{39062500}$	
	$\langle 320 100 \rangle = -\frac{\sqrt{6}}{480}$	$\langle 320 200 \rangle = -\frac{32\sqrt{3}}{9375}$	$\langle 320 400 \rangle = -\frac{128\sqrt{6}}{1764735}$	$\langle 320 500 \rangle = -\frac{5\sqrt{30}}{196608}$	$\langle 320 600 \rangle = -\frac{32}{295245}$	$\langle 320 700 \rangle = -\frac{392\sqrt{42}}{29296875}$
			$\langle 320 420 \rangle = -\frac{13824\sqrt{6}}{4117715}$	$\langle 320 520 \rangle = -\frac{675\sqrt{21}}{802816}$	$\langle 320 620 \rangle = -\frac{9472\sqrt{14}}{14467005}$	$\langle 320 720 \rangle = -\frac{7371\sqrt{14}}{15625000}$
	$\langle 321 421 \rangle = -\frac{6912\sqrt{6}}{4117715}$	$\langle 321 521 \rangle = -\frac{675\sqrt{21}}{1605632}$	$\langle 321 621 \rangle = -\frac{4736\sqrt{14}}{14467005}$	$\langle 321 721 \rangle = -\frac{7371\sqrt{14}}{31250000}$		
		$\langle 321 541 \rangle = -\frac{675\sqrt{14}}{3211264}$	$\langle 321 641 \rangle = -\frac{512\sqrt{35}}{4822335}$	$\langle 321 741 \rangle = -\frac{7749\sqrt{770}}{429687500}$		
	$\langle 322 422 \rangle = -\frac{13824\sqrt{6}}{4117715}$	$\langle 322 522 \rangle = -\frac{675\sqrt{21}}{802816}$	$\langle 322 622 \rangle = -\frac{9472\sqrt{14}}{14467005}$	$\langle 322 722 \rangle = -\frac{7371\sqrt{14}}{15625000}$		
		$\langle 322 542 \rangle = -\frac{675\sqrt{7}}{3211264}$	$\langle 322 642 \rangle = -\frac{256\sqrt{70}}{4822335}$	$\langle 322 742 \rangle = -\frac{7749\sqrt{385}}{429687500}$	$\langle 320 640 \rangle = -\frac{512\sqrt{42}}{4822335}$	$\langle 320 740 \rangle = -\frac{7749\sqrt{231}}{214843750}$

$n = 4$

$< 400 320 > = -\frac{128\sqrt{6}}{1764735}$	$< 400 520 > = -\frac{91520\sqrt{14}}{301327047}$	$< 400 620 > = -\frac{6368\sqrt{21}}{41015625}$	$< 400 720 > = -\frac{388039424\sqrt{21}}{3501552321135}$	
$< 410 210 > = -\frac{56\sqrt{10}}{6075}$	$< 410 310 > = -\frac{60288\sqrt{10}}{2941225}$	$< 410 510 > = \frac{2001280\sqrt{2}}{43046721}$	$< 410 610 > = \frac{590424\sqrt{14}}{68359375}$	$< 410 710 > = \frac{20835775744\sqrt{35}}{583592035225}$
		$< 410 530 > = -\frac{20480\sqrt{2}}{35480783}$	$< 410 630 > = -\frac{27264}{68359375}$	$< 410 730 > = -\frac{81242464\sqrt{30}}{1945306845075}$
$< 411 211 > = \frac{28\sqrt{10}}{6075}$	$< 411 311 > = \frac{30144\sqrt{10}}{2941225}$	$< 411 511 > = -\frac{1000640\sqrt{2}}{43046721}$	$< 411 611 > = -\frac{295212\sqrt{14}}{68359375}$	$< 411 711 > = -\frac{10417887872\sqrt{35}}{583592035225}$
		$< 411 531 > = -\frac{40960\sqrt{3}}{100442349}$	$< 411 631 > = -\frac{9088\sqrt{6}}{68359375}$	$< 411 731 > = -\frac{162684928\sqrt{5}}{1945306845075}$
$< 420 100 > = -\frac{104}{28125}$	$< 420 200 > = \frac{2\sqrt{2}}{1215}$	$< 420 300 > = \frac{792\sqrt{3}}{588245}$	$< 420 500 > = \frac{2360\sqrt{5}}{43046721}$	$< 420 600 > = \frac{414\sqrt{6}}{9765625}$
		$< 420 320 > = -\frac{13824\sqrt{6}}{4117715}$	$< 420 520 > = \frac{5081600\sqrt{14}}{2109289329}$	$< 420 620 > = \frac{91008\sqrt{21}}{95703125}$
			$< 420 540 > = -\frac{163840\sqrt{70}}{2109289329}$	$< 420 640 > = -\frac{9216\sqrt{7}}{478515025}$
$< 421 321 > = -\frac{6912\sqrt{6}}{4117715}$	$< 421 521 > = \frac{2540800\sqrt{14}}{2109289329}$	$< 421 621 > = \frac{45504\sqrt{21}}{95703125}$	$< 421 721 > = \frac{1078171136\sqrt{21}}{3501552321135}$	
		$< 421 541 > = -\frac{819200\sqrt{21}}{6327867087}$	$< 421 741 > = \frac{23166976\sqrt{1155}}{12839025177495}$	
$< 422 322 > = \frac{13824\sqrt{6}}{4117715}$	$< 422 522 > = -\frac{5081600\sqrt{14}}{2109289329}$	$< 422 622 > = -\frac{91008\sqrt{21}}{95703125}$	$< 422 722 > = -\frac{2156342272\sqrt{21}}{3501552321135}$	
		$< 422 542 > = -\frac{409600\sqrt{42}}{6327867087}$	$< 422 742 > = \frac{11583488\sqrt{2310}}{12839025177495}$	
$< 430 210 > = -\frac{8\sqrt{10}}{14175}$	$< 430 310 > = \frac{10368\sqrt{10}}{20588675}$	$< 430 510 > = \frac{3200\sqrt{2}}{100442349}$	$< 430 610 > = \frac{648\sqrt{14}}{68359375}$	$< 430 710 > = \frac{3048192\sqrt{35}}{648435615025}$
			$< 430 630 > = \frac{79872}{68359375}$	$< 430 730 > = \frac{7035870424\sqrt{30}}{52523284817025}$
		$< 430 530 > = \frac{1638400\sqrt{2}}{903981141}$	$< 430 650 > = \frac{12288\sqrt{35}}{150390625}$	$< 430 750 > = \frac{873463808\sqrt{105}}{23110245319491}$
$< 431 211 > = -\frac{16\sqrt{15}}{42525}$	$< 431 311 > = \frac{6912\sqrt{15}}{20588675}$	$< 431 511 > = \frac{6400\sqrt{3}}{301327047}$	$< 431 611 > = \frac{432\sqrt{21}}{68359375}$	$< 431 711 > = \frac{1016064\sqrt{210}}{648435615025}$
		$< 431 531 > = \frac{409600\sqrt{2}}{301327047}$	$< 431 631 > = \frac{59904}{68359375}$	$< 431 731 > = \frac{1758969856\sqrt{30}}{17507761605675}$
$< 432 652 > = \frac{18432\sqrt{5}}{107421875}$	$< 432 752 > = \frac{3057123328\sqrt{15}}{38517075532485}$			$< 431 751 > = \frac{486731904\sqrt{42}}{7703415106497}$
$< 433 533 > = -\frac{2048000\sqrt{2}}{903981141}$	$< 433 633 > = -\frac{19968}{13671875}$	$< 433 733 > = -\frac{1758969856\sqrt{30}}{10504656963405}$		
		$< 433 653 > = \frac{12288\sqrt{5}}{107421875}$		

$n = 5$

$< 500 320 > = -\frac{5\sqrt{30}}{196608}$	$< 500 420 > = -\frac{2360\sqrt{5}}{43046721}$	$< 500 620 > = -\frac{33826640\sqrt{105}}{544685910621}$	$< 500 720 > = -\frac{91685\sqrt{105}}{2176782336}$	$< 510 710 > = \frac{708547\sqrt{70}}{181398528}$
$< 510 210 > = -\frac{8768\sqrt{5}}{1058841}$	$< 510 310 > = -\frac{231\sqrt{5}}{16384}$	$< 510 410 > = -\frac{2001280\sqrt{2}}{43046721}$	$< 510 610 > = \frac{4537728960\sqrt{7}}{181561972207}$	$< 510 730 > = -\frac{2975\sqrt{15}}{40310784}$
		$< 510 430 > = -\frac{3200\sqrt{2}}{100442349}$	$< 510 630 > = -\frac{64694400\sqrt{2}}{181561972207}$	$< 511 711 > = -\frac{708547\sqrt{70}}{362797056}$
$< 511 211 > = \frac{4384\sqrt{5}}{1058841}$	$< 511 311 > = \frac{231\sqrt{5}}{32768}$	$< 511 411 > = \frac{1000640\sqrt{2}}{43046721}$	$< 511 611 > = -\frac{2268864480\sqrt{7}}{181561972207}$	$< 511 731 > = -\frac{2975\sqrt{10}}{40310784}$
		$< 511 431 > = -\frac{6400\sqrt{3}}{301327047}$	$< 511 631 > = -\frac{43129600\sqrt{3}}{181561972207}$	$< 520 600 > = \frac{3258720\sqrt{21}}{181561972207}$
$< 520 100 > = -\frac{5\sqrt{11}}{6804}$	$< 520 200 > = \frac{3680\sqrt{7}}{7411887}$	$< 520 300 > = \frac{45\sqrt{42}}{229376}$	$< 520 400 > = \frac{91520\sqrt{14}}{301327047}$	$< 520 620 > = \frac{98092800\sqrt{6}}{25937424601}$
		$< 520 320 > = -\frac{675\sqrt{21}}{802816}$	$< 520 420 > = -\frac{5081600\sqrt{14}}{2109289329}$	$< 520 640 > = -\frac{54720000\sqrt{2}}{181561972207}$
			$< 521 621 > = \frac{49046400\sqrt{6}}{25937424601}$	$< 530 710 > = \frac{637\sqrt{70}}{161243136}$
$< 521 321 > = -\frac{675\sqrt{21}}{1605632}$	$< 521 421 > = -\frac{2540800\sqrt{14}}{2109289329}$	$< 521 641 > = -\frac{18240000\sqrt{15}}{181561972207}$	$< 521 741 > = -\frac{30625\sqrt{330}}{3990767616}$	$< 530 730 > = \frac{145775\sqrt{15}}{408146688}$
		$< 522 422 > = \frac{5081600\sqrt{14}}{2109289329}$	$< 522 622 > = -\frac{98092800\sqrt{6}}{25937424601}$	$< 530 750 > = \frac{153125\sqrt{210}}{71833817088}$
			$< 522 642 > = -\frac{9120000\sqrt{30}}{181561972207}$	$< 531 711 > = \frac{637\sqrt{105}}{241864704}$
$< 530 210 > = -\frac{512\sqrt{5}}{823543}$	$< 530 310 > = \frac{81\sqrt{5}}{458752}$	$< 530 410 > = \frac{20480\sqrt{2}}{33480783}$	$< 530 610 > = \frac{2695680\sqrt{7}}{181561972207}$	$< 531 731 > = \frac{145775\sqrt{15}}{544195584}$
		$< 530 430 > = -\frac{1638400\sqrt{2}}{903981141}$	$< 530 630 > = \frac{372940800\sqrt{2}}{181561972207}$	$< 531 751 > = \frac{153125\sqrt{21}}{239444605696}$
$< 531 211 > = -\frac{512\sqrt{30}}{2470629}$	$< 531 311 > = \frac{27\sqrt{30}}{458752}$	$< 531 411 > = \frac{40960\sqrt{3}}{100442349}$	$< 531 611 > = \frac{898560\sqrt{42}}{181561972207}$	
		$< 531 431 > = -\frac{409600\sqrt{2}}{301327047}$	$< 531 631 > = \frac{279705600\sqrt{2}}{181561972207}$	
			$< 531 651 > = -\frac{230400000\sqrt{7}}{1997181694277}$	
$< 532 652 > = -\frac{23040000\sqrt{10}}{285311670611}$	$< 532 752 > = \frac{214375\sqrt{30}}{47889211392}$	$< 533 733 > = -\frac{728875\sqrt{15}}{1632586752}$	$< 540 720 > = \frac{1715\sqrt{30}}{725594112}$	
$< 533 433 > = \frac{2048000\sqrt{2}}{903981141}$	$< 533 633 > = -\frac{466176000\sqrt{2}}{181561972207}$	$< 533 753 > = \frac{214375\sqrt{30}}{71833817088}$	$< 540 740 > = \frac{1071875\sqrt{55}}{16461916416}$	
		$< 533 653 > = -\frac{15360000\sqrt{10}}{285311670611}$	$< 540 760 > = \frac{37515625\sqrt{330}}{2282719076352}$	
$< 540 320 > = -\frac{135\sqrt{105}}{1605632}$	$< 540 420 > = \frac{163840\sqrt{70}}{2109289329}$	$< 540 620 > = \frac{552960\sqrt{30}}{181561972207}$	$< 541 721 > = \frac{8575}{725594112}$	
		$< 540 640 > = \frac{691200000\sqrt{10}}{1997181694277}$	$< 541 741 > = \frac{3644375\sqrt{55}}{65847665664}$	
$< 541 321 > = -\frac{675\sqrt{14}}{3211264}$	$< 541 421 > = \frac{819200\sqrt{21}}{6327867987}$	$< 541 621 > = \frac{2764800}{181561972207}$	$< 541 761 > = \frac{37515625\sqrt{77}}{1141359538176}$	
		$< 542 422 > = \frac{409600\sqrt{42}}{6327867987}$	$< 542 722 > = \frac{8575\sqrt{2}}{1451188224}$	
			$< 542 742 > = \frac{214375\sqrt{55}}{8230958208}$	
$< 543 643 > = -\frac{34560000\sqrt{10}}{285311670611}$	$< 543 743 > = -\frac{1500625\sqrt{55}}{65847665664}$	$< 543 763 > = \frac{7503125\sqrt{110}}{380453179392}$	$< 542 762 > = \frac{7503125\sqrt{385}}{570679769088}$	
$< 544 644 > = -\frac{138240000\sqrt{10}}{285311670611}$	$< 544 744 > = -\frac{1500625\sqrt{55}}{16461916416}$	$< 544 764 > = \frac{37515625\sqrt{66}}{2282719076352}$		

$< 600 320 > = -\frac{32}{295245}$	$< 600 420 > = -\frac{414\sqrt{6}}{9765625}$	$< 600 520 > = -\frac{3258720\sqrt{21}}{181561972207}$	$< 600 720 > = -\frac{12194800992\sqrt{14}}{116490425612405}$	$< 610 710 > = \frac{12213784164288\sqrt{10}}{582452128062025}$
$< 610 210 > = -\frac{201\sqrt{35}}{89600}$	$< 610 310 > = -\frac{35648\sqrt{35}}{10333575}$	$< 610 410 > = -\frac{590424\sqrt{14}}{68359375}$	$< 610 510 > = -\frac{4537728960\sqrt{7}}{181561972207}$	$< 610 730 > = -\frac{17995074048\sqrt{105}}{582452128062025}$
$< 611 211 > = \frac{201\sqrt{35}}{179200}$	$< 611 311 > = \frac{17824\sqrt{35}}{10333575}$	$< 611 410 > = -\frac{648\sqrt{14}}{68359375}$	$< 610 530 > = -\frac{2695680\sqrt{7}}{181561972207}$	$< 611 730 > = -\frac{6106892082144\sqrt{10}}{582452128062025}$
$< 620 100 > = -\frac{5744\sqrt{21}}{12335145}$	$< 620 200 > = \frac{29\sqrt{12}}{215040}$	$< 611 411 > = \frac{295212\sqrt{14}}{68359375}$	$< 611 511 > = \frac{226886480\sqrt{7}}{181561972207}$	$< 611 711 > = -\frac{17995074048\sqrt{105}}{582452128062025}$
$< 620 100 > = -\frac{5744\sqrt{21}}{12335145}$	$< 620 300 > = \frac{656\sqrt{7}}{2066715}$	$< 611 431 > = -\frac{432\sqrt{21}}{68359375}$	$< 611 531 > = -\frac{898560\sqrt{42}}{181561972207}$	$< 611 731 > = -\frac{17995074048\sqrt{105}}{582452128062025}$
$< 620 100 > = -\frac{5744\sqrt{21}}{12335145}$	$< 620 400 > = \frac{9472\sqrt{14}}{14467005}$	$< 620 300 > = \frac{656\sqrt{7}}{2066715}$	$< 620 400 > = \frac{6368\sqrt{21}}{41015625}$	$< 620 500 > = \frac{33826640\sqrt{105}}{344685916621}$
$< 621 321 > = -\frac{4736\sqrt{14}}{14467005}$	$< 621 421 > = -\frac{45504\sqrt{21}}{95703125}$	$< 621 521 > = -\frac{49046400\sqrt{6}}{25937424601}$	$< 621 721 > = \frac{545774374656}{116490425612405}$	$< 620 700 > = \frac{11441201296\sqrt{3}}{349471276837215}$
$< 622 322 > = \frac{9472\sqrt{14}}{14467005}$	$< 622 422 > = \frac{91008\sqrt{21}}{95703125}$	$< 622 522 > = -\frac{2764800}{181561972207}$	$< 622 722 > = -\frac{44094468096\sqrt{55}}{1281394681736455}$	$< 620 720 > = \frac{1091548749312}{116490425612405}$
$< 630 210 > = -\frac{123\sqrt{10}}{388400}$	$< 630 310 > = \frac{128\sqrt{10}}{3444525}$	$< 622 542 > = -\frac{1382400\sqrt{2}}{181561972207}$	$< 622 742 > = -\frac{22047234048\sqrt{110}}{1281394681736455}$	$< 630 710 > = \frac{3040778496\sqrt{35}}{582452128062025}$
$< 631 211 > = -\frac{41\sqrt{15}}{179200}$	$< 631 311 > = \frac{256\sqrt{15}}{1033575}$	$< 630 410 > = \frac{27264}{68359375}$	$< 630 510 > = \frac{64694400\sqrt{2}}{181561972207}$	$< 630 730 > = \frac{322034786304\sqrt{30}}{582452128062025}$
$< 632 752 > = -\frac{62817140736\sqrt{15}}{1281394681736455}$	$< 633 311 > = \frac{256\sqrt{15}}{1033575}$	$< 630 430 > = -\frac{79872}{68359375}$	$< 630 530 > = -\frac{372940800\sqrt{2}}{181561972207}$	$< 630 750 > = -\frac{5982584832\sqrt{105}}{256278936347291}$
$< 633 433 > = \frac{19968}{13671875}$	$< 633 533 > = \frac{466176000\sqrt{2}}{181561972207}$	$< 631 411 > = \frac{9088\sqrt{6}}{68359375}$	$< 631 511 > = \frac{43129600\sqrt{3}}{181561972207}$	$< 631 711 > = \frac{1013599832\sqrt{210}}{582452128062025}$
$< 640 320 > = -\frac{512\sqrt{42}}{4822335}$	$< 640 420 > = \frac{9216\sqrt{7}}{478515625}$	$< 631 431 > = -\frac{59904}{68359375}$	$< 631 531 > = -\frac{279705600\sqrt{2}}{181561972207}$	$< 631 731 > = \frac{241526089728\sqrt{30}}{582452128062025}$
$< 641 321 > = -\frac{512\sqrt{35}}{4822335}$	$< 641 421 > = \frac{1536\sqrt{210}}{478515625}$	$< 640 540 > = -\frac{1997181694277}{1997181694277}$	$< 640 760 > = -\frac{1147095613440\sqrt{735}}{36647887897662613}$	$< 631 751 > = -\frac{8973877248\sqrt{42}}{256278936347291}$
$< 642 322 > = -\frac{256\sqrt{70}}{4822335}$	$< 642 422 > = \frac{1536\sqrt{105}}{478515625}$	$< 641 521 > = \frac{18240000\sqrt{15}}{181561972207}$	$< 641 721 > = \frac{567415296\sqrt{10}}{116490425612405}$	
$< 643 543 > = \frac{34560000\sqrt{10}}{285311670611}$	$< 643 743 > = -\frac{1340004169728\sqrt{22}}{14095341499101005}$	$< 642 522 > = \frac{9120000\sqrt{30}}{181561972207}$	$< 642 722 > = \frac{567415296\sqrt{5}}{116490425612405}$	
$< 644 544 > = \frac{138240000\sqrt{10}}{285311670611}$	$< 643 763 > = -\frac{1376514736128\sqrt{11}}{36647887897662613}$	$< 642 542 > = -\frac{276480000\sqrt{10}}{1997181694277}$	$< 642 742 > = \frac{1531433336832\sqrt{22}}{14095341499101005}$	
$< 650 430 > = -\frac{12288\sqrt{35}}{130390625}$	$< 644 764 > = -\frac{229419122688\sqrt{165}}{36647887897662613}$	$< 641 541 > = -\frac{587520000\sqrt{10}}{1997181694277}$	$< 641 761 > = -\frac{229419122688\sqrt{770}}{36647887897662613}$	
$< 651 431 > = -\frac{18432\sqrt{14}}{150390625}$	$< 650 530 > = \frac{76800000\sqrt{70}}{1997181694277}$	$< 650 730 > = \frac{295034880\sqrt{42}}{256278936347291}$	$< 642 762 > = -\frac{36647887897662613}{36647887897662613}$	
$< 652 432 > = -\frac{18432\sqrt{5}}{107421875}$	$< 651 531 > = \frac{230400000\sqrt{7}}{1997181694277}$	$< 650 750 > = \frac{1070622572544\sqrt{3}}{3331626172514783}$	$< 642 762 > = -\frac{36647887897662613}{36647887897662613}$	
	$< 651 731 > = \frac{177020928\sqrt{105}}{256278936347291}$	$< 651 751 > = \frac{4817801576448\sqrt{3}}{16658130862573915}$	$< 642 762 > = -\frac{36647887897662613}{36647887897662613}$	
	$< 652 532 > = \frac{23040000\sqrt{10}}{285311670611}$	$< 652 732 > = \frac{619573248\sqrt{6}}{256278936347291}$	$< 652 752 > = \frac{3211867717632\sqrt{3}}{16658130862573915}$	

$n = 6$ continued ...			
$< 653 433 > = -$	$\frac{12288\sqrt{6}}{107421875}$	$< 653 533 > =$	$\frac{15360000\sqrt{10}}{285311670611}$
		$< 653 733 > =$	$\frac{413048832\sqrt{6}}{256278936347291}$
		$< 653 753 > =$	$\frac{535311286272\sqrt{3}}{16658130862573915}$
$< 654 754 > = -$	$\frac{321186717632\sqrt{3}}{16658130862573915}$		
$< 655 755 > = -$	$\frac{160593385816\sqrt{3}}{3331626172514783}$		

$n = 7$

$< 700 320 > = -\frac{392\sqrt{42}}{29296875}$	$< 700 520 > = -\frac{4189512\sqrt{7}}{129687123005}$	$< 700 620 > = -\frac{18865\sqrt{2}}{362797056}$	$< 700 610 > = -\frac{11441201296\sqrt{3}}{349471276837215}$
$< 710 210 > = -\frac{2926784\sqrt{14}}{1076168025}$	$< 710 310 > = -\frac{310191\sqrt{14}}{78126000}$	$< 710 510 > = -\frac{708547\sqrt{70}}{181398528}$	$< 710 610 > = -\frac{12213784164288\sqrt{10}}{582452128062025}$
$< 711 211 > = \frac{1463392\sqrt{14}}{1076168025}$	$< 711 311 > = \frac{310191\sqrt{14}}{156250000}$	$< 710 430 > = -\frac{3048192\sqrt{35}}{648435615025}$	$< 710 630 > = -\frac{3040778496\sqrt{35}}{582452128062025}$
$< 720 100 > = -\frac{3299\sqrt{21}}{8847360}$	$< 720 200 > = \frac{63584\sqrt{42}}{645700815}$	$< 711 411 > = \frac{10417887872\sqrt{35}}{5835920535225}$	$< 711 611 > = \frac{6106892082144\sqrt{10}}{582452128062025}$
		$< 711 431 > = -\frac{1016064\sqrt{210}}{648435615025}$	$< 711 631 > = -\frac{1013592832\sqrt{210}}{582452128062025}$
		$< 720 300 > = \frac{1809\sqrt{7}}{7812500}$	$< 720 500 > = \frac{91685\sqrt{105}}{2176782336}$
		$< 720 320 > = -\frac{7371\sqrt{14}}{15625000}$	$< 720 520 > = -\frac{1008175\sqrt{6}}{544195584}$
$< 721 321 > = -\frac{7371\sqrt{14}}{31250000}$	$< 721 421 > = -\frac{1078171136\sqrt{21}}{3501552321135}$	$< 721 521 > = -\frac{1008175\sqrt{6}}{1088391168}$	$< 720 600 > = \frac{12104800992\sqrt{14}}{116490425612405}$
$< 722 322 > = \frac{7371\sqrt{14}}{13625000}$	$< 722 422 > = \frac{2156342272\sqrt{21}}{3501552321135}$	$< 721 541 > = -\frac{8575}{725594112}$	$< 720 620 > = -\frac{1091548749312}{116490425612405}$
$< 730 210 > = -\frac{541184\sqrt{3}}{1076168025}$	$< 730 310 > = \frac{567\sqrt{3}}{39062500}$	$< 722 522 > = \frac{1008175\sqrt{6}}{544195584}$	$< 720 640 > = -\frac{1715\sqrt{30}}{725594112}$
		$< 722 542 > = -\frac{8575\sqrt{2}}{1451188224}$	
		$< 730 410 > = \frac{81342464\sqrt{30}}{1945306845075}$	$< 730 610 > = \frac{17995074048\sqrt{105}}{582452128062025}$
		$< 730 430 > = -\frac{7035879424\sqrt{30}}{52523284817025}$	$< 730 630 > = -\frac{322034786304\sqrt{30}}{582452128062025}$
$< 731 211 > = -\frac{541184\sqrt{3}}{1076168025}$	$< 731 311 > = \frac{567\sqrt{3}}{39062500}$	$< 731 411 > = \frac{162684928\sqrt{5}}{1945306845075}$	$< 730 650 > = -\frac{295034880\sqrt{42}}{256278936347291}$
		$< 731 431 > = -\frac{1758969856\sqrt{30}}{17507761605675}$	$< 731 611 > = \frac{17995074048\sqrt{70}}{582452128062025}$
$< 732 652 > = -\frac{619573248\sqrt{6}}{256278936347291}$	$< 733 533 > = \frac{728875\sqrt{15}}{1632586752}$	$< 733 633 > = \frac{80508096576\sqrt{30}}{116490425612405}$	$< 731 631 > = -\frac{241526089728\sqrt{30}}{582452128062025}$
$< 733 433 > = \frac{1758969856\sqrt{30}}{10504656963405}$		$< 733 653 > = -\frac{413048832\sqrt{6}}{256278936347291}$	$< 731 651 > = -\frac{177020928\sqrt{105}}{256278936347291}$
$< 740 320 > = -\frac{7749\sqrt{231}}{214843750}$	$< 740 420 > = -\frac{23166976\sqrt{154}}{4279675059165}$	$< 740 520 > = \frac{30625\sqrt{11}}{665127936}$	
$< 741 321 > = -\frac{7749\sqrt{770}}{429687500}$	$< 741 421 > = -\frac{23166976\sqrt{155}}{12839025177495}$	$< 740 540 > = -\frac{1071875\sqrt{55}}{16461916416}$	$< 740 620 > = \frac{44094468096\sqrt{66}}{1281394681736455}$
		$< 741 521 > = \frac{30625\sqrt{330}}{3990767616}$	$< 741 621 > = \frac{44094468096\sqrt{55}}{1281394681736455}$
		$< 741 541 > = -\frac{3644375\sqrt{55}}{65847665664}$	$< 741 641 > = -\frac{3254295840768\sqrt{22}}{14095341499101005}$
$< 742 322 > = -\frac{7749\sqrt{385}}{429687500}$	$< 742 422 > = -\frac{11583488\sqrt{2310}}{12839025177495}$	$< 742 522 > = \frac{30625\sqrt{165}}{3990767616}$	$< 742 622 > = \frac{22047234048\sqrt{110}}{1281394681736455}$
		$< 742 542 > = -\frac{214375\sqrt{55}}{8230958208}$	$< 742 642 > = -\frac{1531433336832\sqrt{22}}{14095341499101005}$
$< 743 543 > = \frac{1500625\sqrt{55}}{65847665664}$	$< 743 643 > = \frac{1340004169728\sqrt{22}}{14095341499101005}$		
$< 744 544 > = \frac{1500625\sqrt{55}}{16461916416}$	$< 744 644 > = \frac{5360016678012\sqrt{22}}{14095341499101005}$		

$n = 7$ continued ...

$\langle 750 430 \rangle = -\frac{873468898\sqrt{105}}{23110245319491}$	$\langle 750 530 \rangle = -\frac{153125\sqrt{210}}{71833817088}$	$\langle 750 630 \rangle = \frac{5982584832\sqrt{105}}{256278936347291}$
$\langle 751 431 \rangle = -\frac{436731904\sqrt{42}}{7703415106497}$	$\langle 751 531 \rangle = -\frac{153125\sqrt{21}}{23944605696}$	$\langle 751 631 \rangle = \frac{1070622572544\sqrt{3}}{3331626172514783}$
$\langle 752 432 \rangle = -\frac{3057123328\sqrt{15}}{38517075532485}$	$\langle 752 532 \rangle = -\frac{214375\sqrt{30}}{47889211392}$	$\langle 752 632 \rangle = \frac{8973877248\sqrt{42}}{256278936347291}$
$\langle 753 433 \rangle = -\frac{6114246656\sqrt{15}}{115551226597455}$	$\langle 753 533 \rangle = -\frac{214375\sqrt{30}}{71833817088}$	$\langle 753 633 \rangle = \frac{4817801576448\sqrt{3}}{16658130862573915}$
$\langle 754 654 \rangle = \frac{3211867717632\sqrt{3}}{16658130862573915}$		$\langle 754 655 \rangle = \frac{62817140736\sqrt{15}}{1281394681736455}$
$\langle 755 655 \rangle = \frac{1605933858816\sqrt{3}}{3331626172514783}$		$\langle 752 652 \rangle = -\frac{3211867717632\sqrt{3}}{16658130862573915}$
$\langle 760 540 \rangle = -\frac{37515625\sqrt{330}}{2282719076352}$		$\langle 753 653 \rangle = \frac{41878003824\sqrt{15}}{1281394681736455}$
$\langle 761 541 \rangle = -\frac{37515625\sqrt{77}}{1141359538176}$	$\langle 760 640 \rangle = \frac{1147095613440\sqrt{33}}{36647887897662613}$	$\langle 753 653 \rangle = -\frac{535311286272\sqrt{3}}{16658130862573915}$
$\langle 762 542 \rangle = -\frac{7503125\sqrt{385}}{570679769088}$	$\langle 761 641 \rangle = \frac{229419122688\sqrt{770}}{36647887897662613}$	
$\langle 763 543 \rangle = -\frac{7503125\sqrt{410}}{380453170392}$	$\langle 762 642 \rangle = \frac{458838245376\sqrt{154}}{36647887897662613}$	
$\langle 764 544 \rangle = -\frac{37515625\sqrt{66}}{2282719076352}$	$\langle 763 643 \rangle = \frac{1376514736128\sqrt{11}}{36647887897662613}$	
	$\langle 764 644 \rangle = \frac{229419122688\sqrt{165}}{36647887897662613}$	

Table 5: Non-zero, first order coupling coefficients up to $n=7$ in $\frac{\mu^2 Z^2}{a}$ units,

that is to say, $\psi_{n,l,m}^{(1)} = \sum_{(n',l') \neq (n,l)} \langle n'l'm|nlm \rangle \frac{\mu^2 Z^2}{a} \psi_{n',l',m}^{(0)}$.

Only positive m -values are tabulated, their negative counterparts giving the same coupling coefficients. Note that, all numbers being real, $\langle n'l'm|nlm \rangle = \langle nlm|n'l'm \rangle$