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Smearred Coulomb potential orbitals for the electron-nucleus mean field configuration interaction method

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Abstract

We propose to use the eigenfunctions of a one-electron model Hamiltonian to perform electron-nucleus mean field configuration interaction (EN-MFCI) calculations. The potential energy of our model Hamiltonian 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 limit of small amplitude vibration (Gaussian function width close to zero). Since the parameter controlling the width of the potential factorizes the perturbative corrections to the eigenfunctions, we propose to simply add the latter to standard basis sets, leaving it to molecular orbital calculations to optimize this free parameter. The new functions have been fitted with Gaussian-type orbitals (GTO) with mixed Cartesian prefactors to calculate multicenter integrals efficiently. The BDF code has been modified to accept contracted GTO having such mixed Cartesian prefactors.

1 Introduction

This paper is dedicated to Prof. Graham Chandler, whose 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 latter⁸⁻¹⁰ 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, these additional functions introduce linear dependencies with the initial orbitals and span 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 sets for the EN-MFCI method, able to describe the smeared electronic cloud of oscillating nuclei in a molecular system.

We propose to use the eigenfunctions of a 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 tend 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

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

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

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

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,

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

Since this potential is not bounded from below, we will just apply Rayleigh-Schrödinger perturbation theory to first order, to get corrections with respect to the hydrogenoid atom eigenstates.

2 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 in¹³, 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 $L_{n-l-1}^{2l+1} \left(\frac{2\mu Z r}{n} \right) = L_{n-l'-3}^{2l'+5} \left(\frac{2\mu Z r}{n} \right)$ can be expanded as a linear combination of generalized Laguerre polynomial $L_i^{2l'+1} \left(\frac{2\mu Z r}{n} \right)$ with $i \leq n - l' - 3$. All these polynomials are orthogonal to $L_{n-l'-1}^{2l'+1} \left(\frac{2\mu Z r}{n} \right)$ for the measure $\left(\frac{2\mu Z r}{n} \right)^{(2l'+1)} \exp \left(-\frac{2\mu Z r}{n} \right)$ 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 corrections at the first order 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.

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

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

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

the radial integral being proportional to $\mu^3 Z^3$ (because of the $\frac{1}{r^3}$ -term, when we make the change of variables $x = 2\mu Z r$), 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 explaining that the first order matrix, Eq.(15), is 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 clearly 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”).

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

3 Application to EN-MFCI calculations

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 be conveniently chosen to be, $c = \mu Z$ and $b = \frac{\mu Z}{a}$. Since the product $b \times c$ factorizes the first order perturbative component of the approximate DHOs, we propose to simply add the functions made of these corrective terms to standard basis sets, leaving 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 product, $b \cdot c$, and consequently, if c is given, the free parameter 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, more simply indexed by j . The u_i, v_j 's are scalar coefficients. To save the specific optimization of the $b_j \cdot c_j$ values for each $DHO_j(c_j)$, we will just use the v_j 's values. That is to say, the c_j being fixed, the b_j will implicitly correspond to $b_j = \frac{v_j}{c_j}$.

It remains 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 have adopted a strategy similar to that of the SMILES module¹⁴ that can be included in the MOLPRO quantum chemistry package¹⁵ to deal with STOs. It consists in fitting $DHO^{(1)}$ by GTOs.

The new functions have been fitted with Gaussian-type orbitals (GTO) with mixed Carte-

sian prefactors. The BDF code has been modified to accept contracted GTO having such mixed Cartesian prefactors.

4 Conclusion

In this study, 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 was hoped that these approximate eigenstates could be appropriate to describe the electron density of the effective electronic Hamiltonians solved in the EN-MFCI method.

Taking advantage of the remarkable fact that, one and the same expression, namely $\frac{\mu^2 Z^2}{a}$, is in factor of the first order correction to any approximate eigenfunction, we have proposed to add such first order corrective functions ($DHO^{(1)}$), to standard basis sets, rather than the approximate eigenfunctions (DHO) themselves. Doing so, we just have to optimize for each extra function a single parameter, $\mu \cdot Z$, controlling the diffuse character of the function. The free parameter a is implicitly determined by the molecular orbital calculation.

For practical purposes, the infinite series expansion of the first order corrective functions have been truncated to $n = 7$, and reexpressed in terms of GTOs to compute multicenter integrals, as in the SMILES program which deals with multicenter integrals of STOs¹⁴.

A hyperbolic cosine factor can be associated to ETO to provide a “double zeta” character to a minimal basis set¹⁶. This can be considered for DHO, as well. However, one can also combine different sets of DHO corresponding to atoms at different ionization states, for example, to obtain proper multi-zeta basis sets.

Beside the application to the EN-MFCI method, these orbitals could be useful for “clamped nuclei” quantum chemistry calculations, as they can be regarded as naturally “hybridized”

(unlike spherical harmonics STO). One can develop a battery of model Hamiltonian adapted to one or several bond directions (whatever a chemical bond might be from the quantum mechanical point of view) and obtain their first order approximate eigenfunctions by following the approach presented in this paper. For example, different shapes of Coulomb potentials could provide different model Hamiltonians for the sp, sp², or sp³ hybridization of a carbon atom, and in turn, relevant naturally-hybridized orbital eigenfunction basis sets.

Another potential application for “clamped nuclei” quantum chemistry is to save on polarization orbital sets, since high angular momentum atomic primitives are already contracted within our orbitals.

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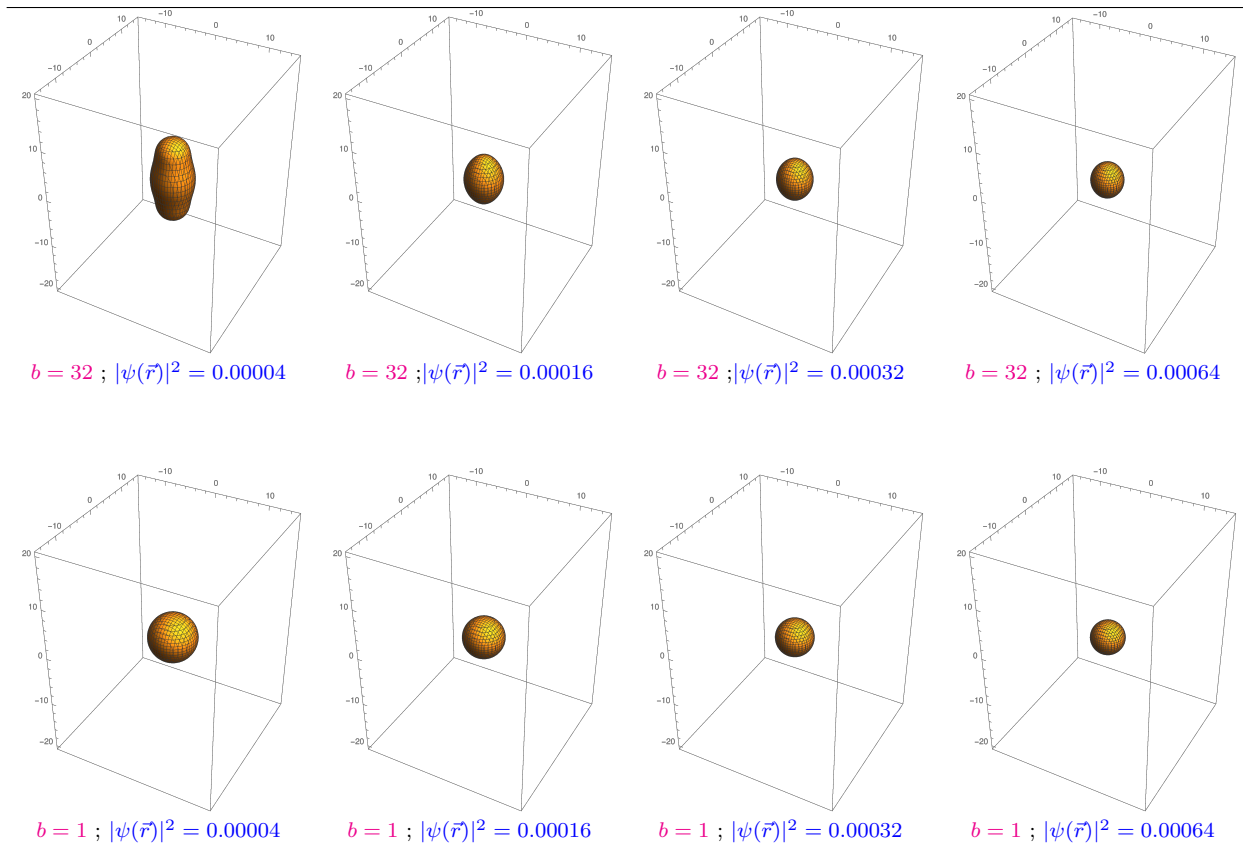


Figure 1: Comparison of hydrogen smeared Coulomb potential 1s orbital squared density levels.

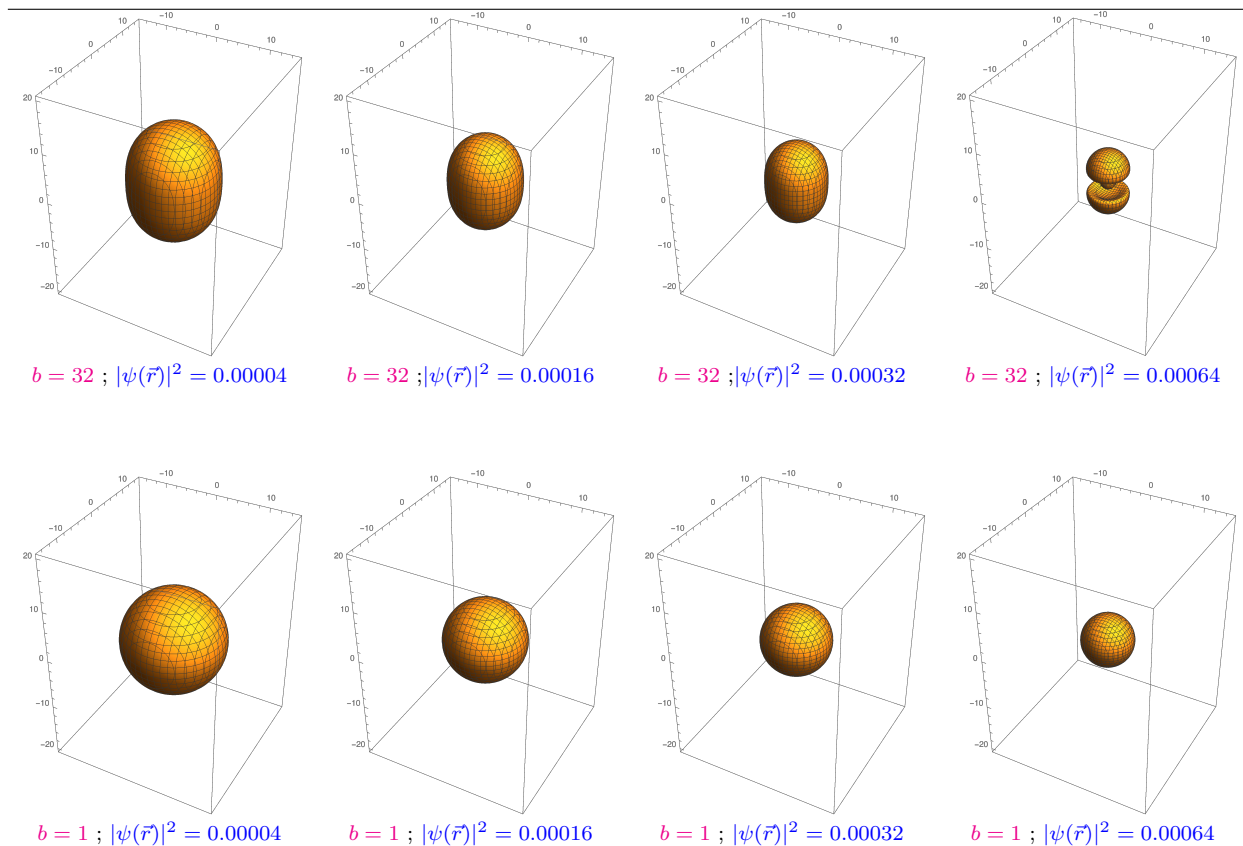


Figure 2: Comparison of hydrogen smeared Coulomb potential 2s orbital squared density levels.

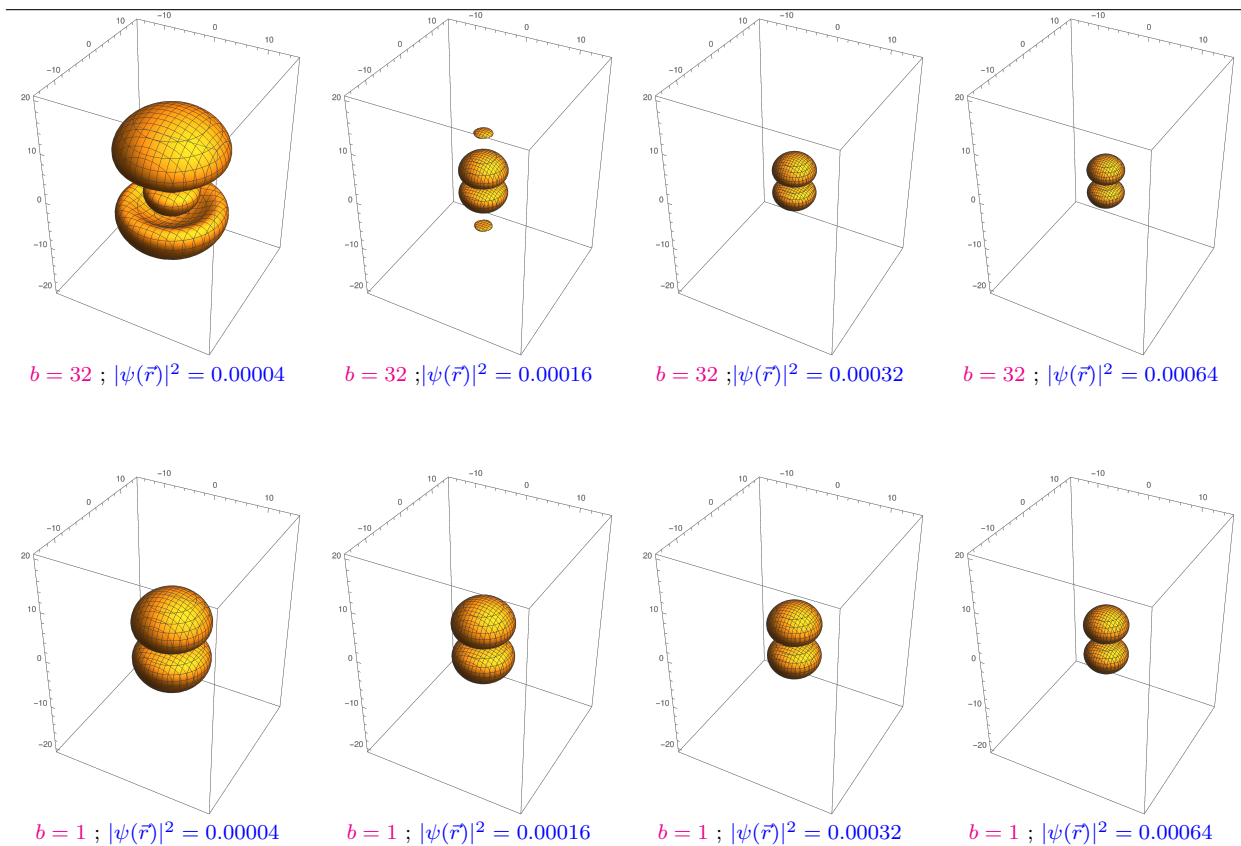


Figure 3: Comparison of hydrogen smeared Coulomb potential $2p_z$ orbital squared density levels.

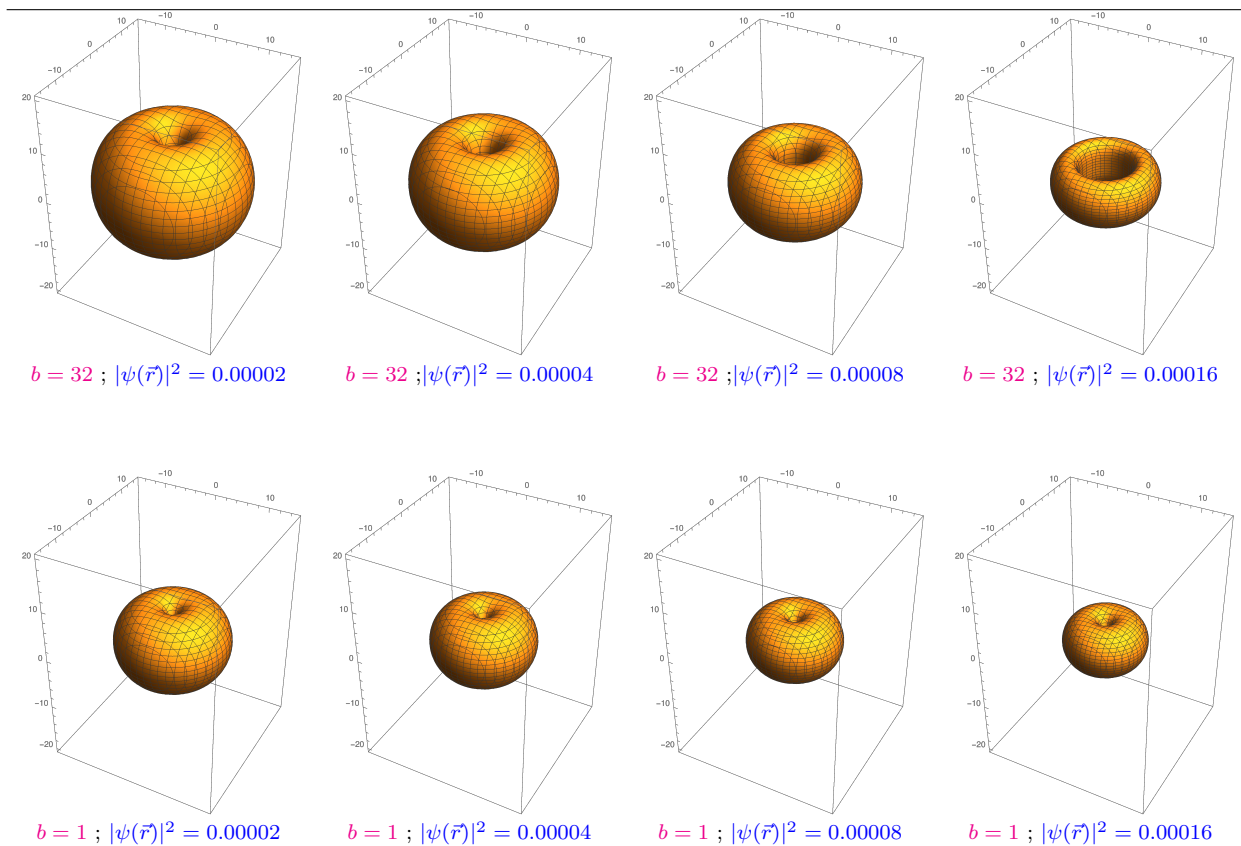


Figure 4: Comparison of hydrogen smeared Coulomb potential $2p_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

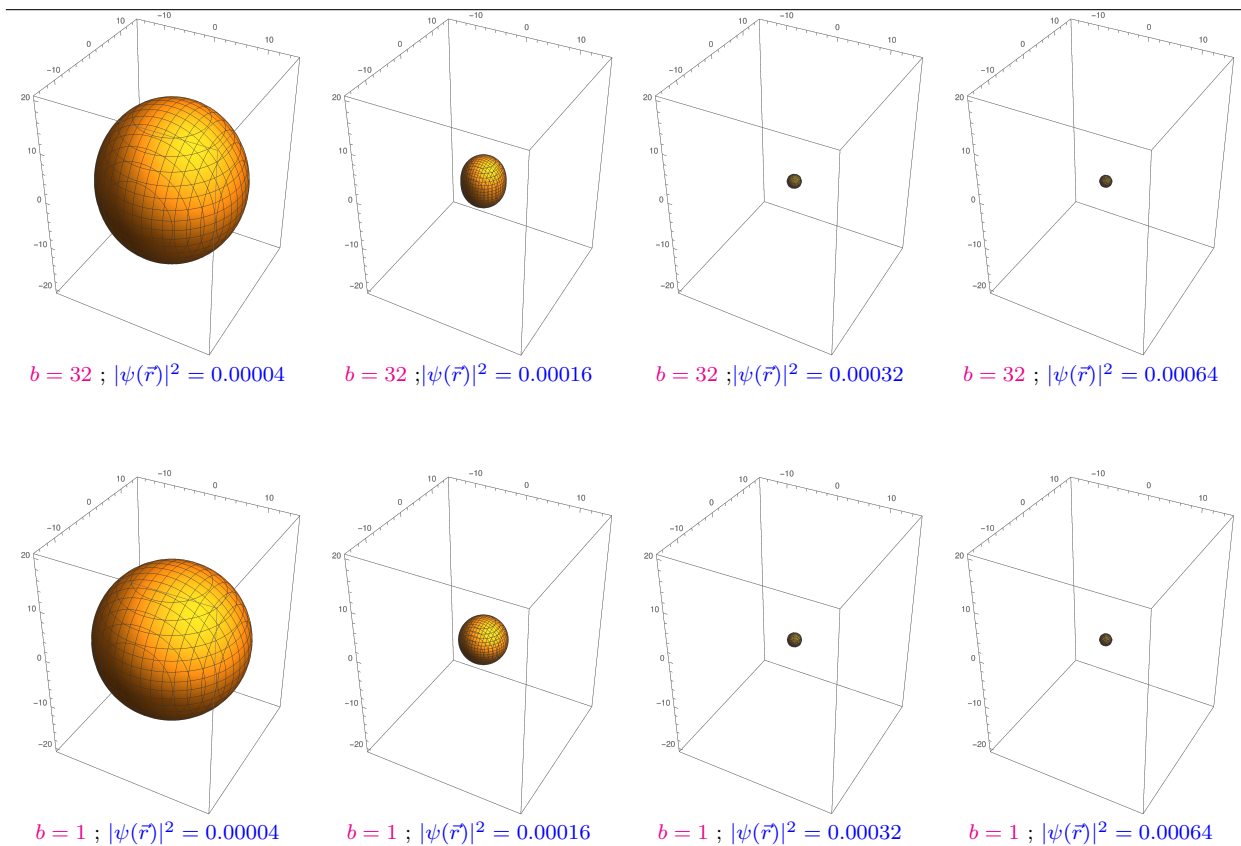


Figure 5: Comparison of hydrogen smeared Coulomb potential 3s orbital squared density levels.

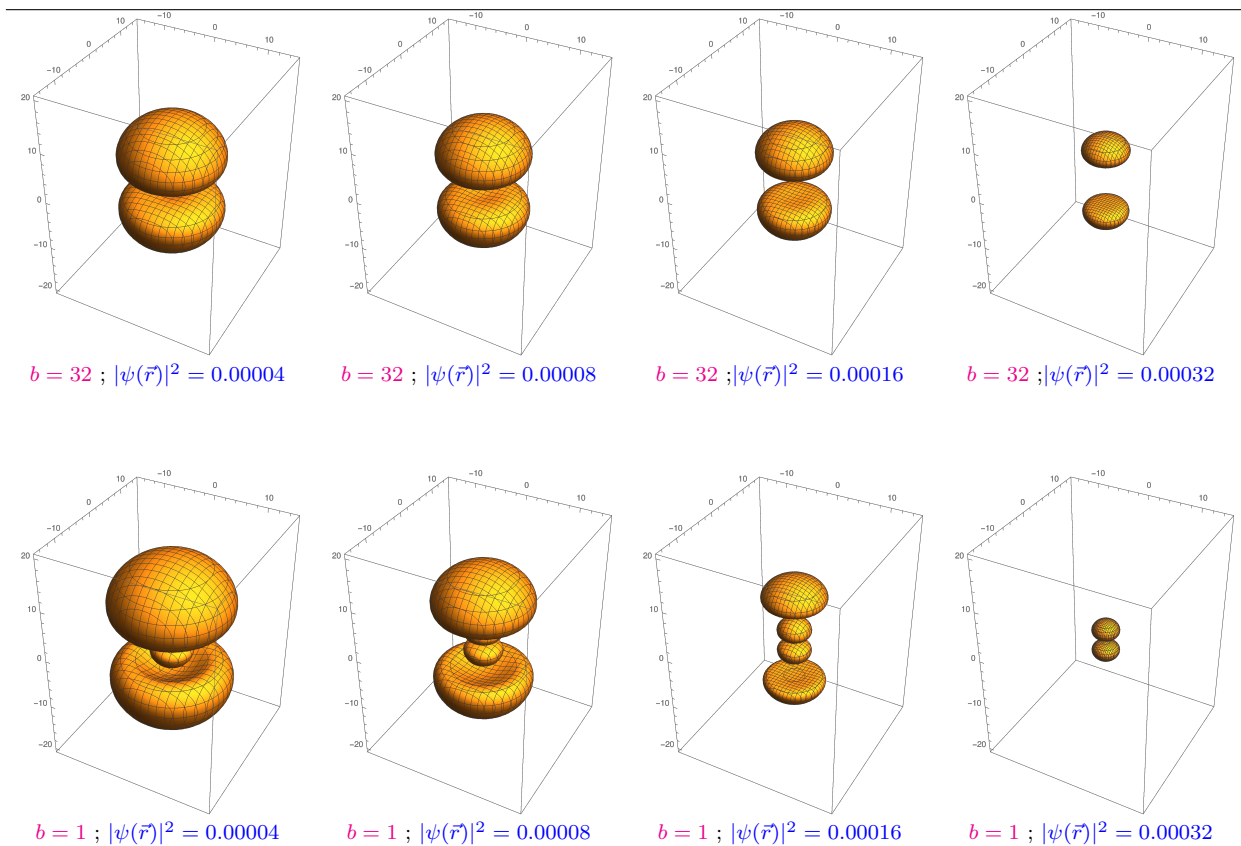


Figure 6: Comparison of hydrogen smeared Coulomb potential $3p_z$ orbital squared density levels.

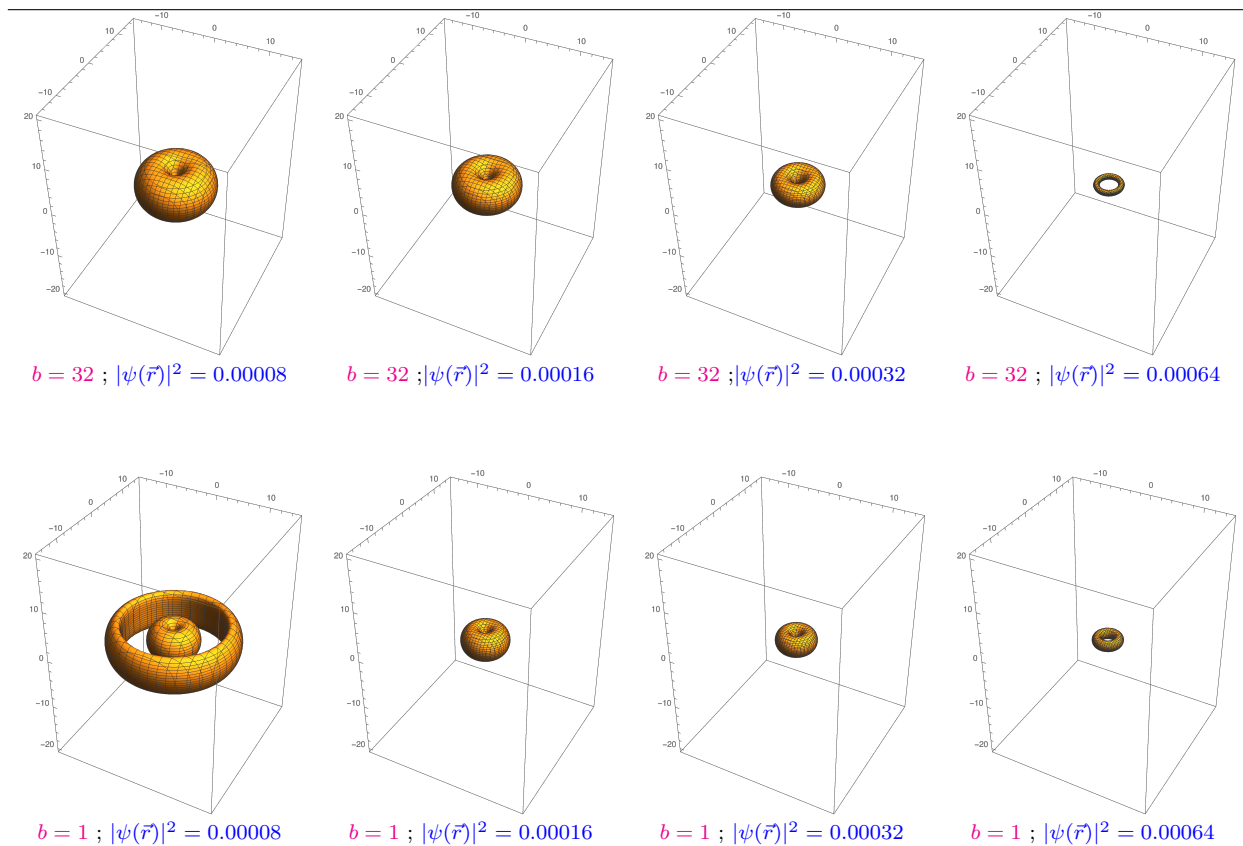


Figure 7: Comparison of hydrogen smeared Coulomb potential $3p_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

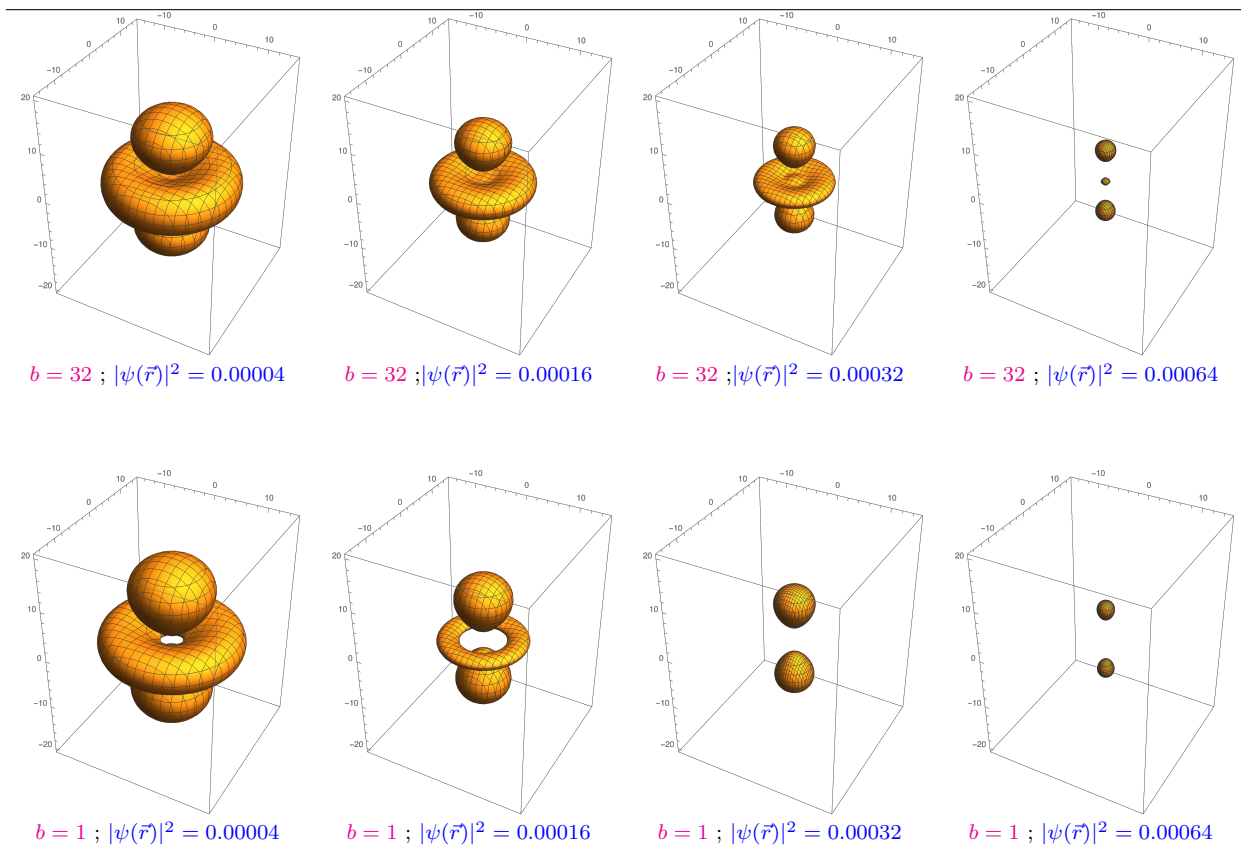


Figure 8: Comparison of hydrogen smeared Coulomb potential $3d_{z^2}$ orbital squared density levels.

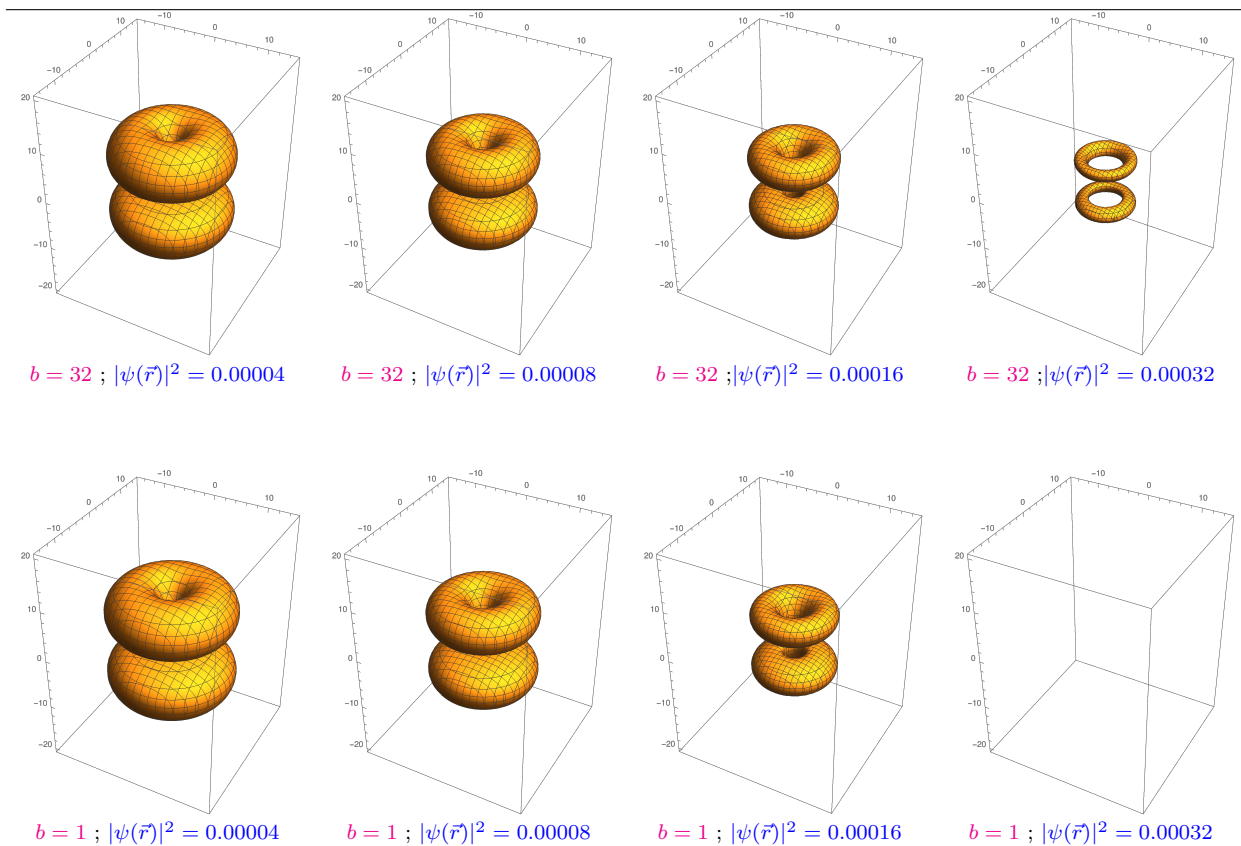


Figure 9: Comparison of hydrogen smeared Coulomb potential $3d_{\pm 1}$ ($m = \pm 1$) orbital squared density levels.

Appendix: First order corrected eigenstates up to n=7

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

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

$\langle 400 320 \rangle = -\frac{128\sqrt{6}}{1764735}$	$\langle 400 520 \rangle = -\frac{91520\sqrt{14}}{301327047}$	$\langle 400 620 \rangle = -\frac{6368\sqrt{21}}{41015625}$	$\langle 400 720 \rangle = -\frac{388039424\sqrt{21}}{3501552321135}$	$\langle 410 710 \rangle = \frac{2083577574\sqrt{35}}{5835920335225}$
$\langle 410 210 \rangle = -\frac{56\sqrt{10}}{6075}$	$\langle 410 310 \rangle = -\frac{60288\sqrt{10}}{2941225}$	$\langle 410 510 \rangle = \frac{2001280\sqrt{2}}{43046721}$	$\langle 410 610 \rangle = \frac{590424\sqrt{14}}{68359375}$	$\langle 410 730 \rangle = -\frac{81349464\sqrt{30}}{1945306845075}$
$\langle 411 211 \rangle = \frac{28\sqrt{10}}{6075}$	$\langle 411 311 \rangle = \frac{30144\sqrt{10}}{2941225}$	$\langle 411 530 \rangle = -\frac{20480\sqrt{2}}{35480783}$	$\langle 411 630 \rangle = -\frac{27264}{68359375}$	$\langle 411 711 \rangle = -\frac{1041788782\sqrt{35}}{3835920335225}$
$\langle 420 100 \rangle = -\frac{104}{28125}$	$\langle 420 200 \rangle = \frac{2\sqrt{2}}{1215}$	$\langle 411 531 \rangle = -\frac{40960\sqrt{3}}{100442349}$	$\langle 411 631 \rangle = -\frac{9088\sqrt{6}}{68359375}$	$\langle 411 731 \rangle = -\frac{162684928\sqrt{5}}{1945306845075}$
$\langle 421 321 \rangle = -\frac{6912\sqrt{6}}{4117715}$	$\langle 421 521 \rangle = \frac{2540800\sqrt{14}}{2109289329}$	$\langle 420 300 \rangle = \frac{792\sqrt{3}}{588245}$	$\langle 420 500 \rangle = \frac{2360\sqrt{5}}{43046721}$	$\langle 420 600 \rangle = \frac{414\sqrt{6}}{9765625}$
$\langle 422 322 \rangle = \frac{13824\sqrt{6}}{4117715}$	$\langle 421 621 \rangle = \frac{45504\sqrt{21}}{95703125}$	$\langle 420 320 \rangle = -\frac{13824\sqrt{6}}{4117715}$	$\langle 420 520 \rangle = \frac{5081600\sqrt{14}}{2109289329}$	$\langle 420 620 \rangle = \frac{91008\sqrt{21}}{95703125}$
$\langle 430 210 \rangle = -\frac{8\sqrt{10}}{14175}$	$\langle 421 541 \rangle = -\frac{819200\sqrt{21}}{6327867987}$	$\langle 421 641 \rangle = -\frac{1536\sqrt{210}}{478515625}$	$\langle 421 741 \rangle = \frac{23166976\sqrt{1155}}{12839025177495}$	$\langle 420 640 \rangle = -\frac{6216\sqrt{7}}{478515625}$
$\langle 431 211 \rangle = -\frac{16\sqrt{15}}{42525}$	$\langle 422 522 \rangle = -\frac{5081600\sqrt{14}}{2109289329}$	$\langle 422 642 \rangle = -\frac{1536\sqrt{105}}{478515625}$	$\langle 422 722 \rangle = -\frac{2156342272\sqrt{21}}{3501552321135}$	$\langle 430 710 \rangle = \frac{3048192\sqrt{35}}{648435615025}$
$\langle 432 652 \rangle = \frac{18432\sqrt{5}}{107421875}$	$\langle 422 542 \rangle = -\frac{409600\sqrt{42}}{6327867987}$	$\langle 430 510 \rangle = \frac{3200\sqrt{2}}{100442349}$	$\langle 422 742 \rangle = \frac{11583488\sqrt{2310}}{12839025177495}$	$\langle 430 730 \rangle = \frac{7035879424\sqrt{30}}{52523284817025}$
$\langle 433 533 \rangle = -\frac{2048000\sqrt{2}}{903981141}$	$\langle 430 310 \rangle = \frac{10368\sqrt{10}}{20688675}$	$\langle 430 530 \rangle = \frac{1638400\sqrt{2}}{903981141}$	$\langle 430 610 \rangle = \frac{648\sqrt{14}}{68359375}$	$\langle 430 750 \rangle = \frac{873463808\sqrt{105}}{23110245319491}$
	$\langle 431 311 \rangle = \frac{6912\sqrt{15}}{20688675}$	$\langle 431 511 \rangle = \frac{6400\sqrt{3}}{301327047}$	$\langle 431 611 \rangle = \frac{432\sqrt{21}}{68359375}$	$\langle 431 711 \rangle = \frac{1016064\sqrt{210}}{648435615025}$
	$\langle 432 752 \rangle = \frac{3057123328\sqrt{15}}{38517075532485}$	$\langle 431 531 \rangle = \frac{409600\sqrt{2}}{301327047}$	$\langle 431 631 \rangle = \frac{59904}{68359375}$	$\langle 431 731 \rangle = \frac{1758969856\sqrt{30}}{17507761606675}$
	$\langle 433 633 \rangle = -\frac{19968}{13671875}$	$\langle 433 733 \rangle = -\frac{1758969856\sqrt{30}}{10504656963405}$	$\langle 431 651 \rangle = \frac{18432\sqrt{14}}{150390625}$	$\langle 431 751 \rangle = \frac{436731904\sqrt{42}}{7703415106497}$
	$\langle 433 653 \rangle = \frac{12288\sqrt{5}}{107421875}$	$\langle 433 753 \rangle = \frac{6114246656\sqrt{15}}{115551226597455}$		

$\langle 500 320 \rangle = -\frac{5\sqrt{30}}{196608}$	$\langle 500 620 \rangle = -\frac{33526640\sqrt{105}}{544685916621}$	$\langle 500 720 \rangle = -\frac{91685\sqrt{105}}{2176782336}$	$\langle 510 710 \rangle = \frac{708547\sqrt{70}}{181398528}$
$\langle 510 210 \rangle = -\frac{8768\sqrt{5}}{1058841}$	$\langle 510 410 \rangle = -\frac{2001280\sqrt{2}}{43046721}$	$\langle 510 610 \rangle = \frac{4537728960\sqrt{7}}{181561972207}$	$\langle 510 730 \rangle = -\frac{2975\sqrt{15}}{40310784}$
$\langle 511 211 \rangle = \frac{4384\sqrt{5}}{1058841}$	$\langle 510 430 \rangle = -\frac{3200\sqrt{2}}{100442349}$	$\langle 510 630 \rangle = -\frac{46494400\sqrt{2}}{181561972207}$	$\langle 511 711 \rangle = -\frac{708547\sqrt{70}}{362797056}$
$\langle 520 100 \rangle = -\frac{5\sqrt{11}}{6804}$	$\langle 511 411 \rangle = \frac{1000640\sqrt{2}}{43046721}$	$\langle 511 611 \rangle = -\frac{2268864480\sqrt{7}}{181561972207}$	$\langle 511 731 \rangle = -\frac{2975\sqrt{10}}{40310784}$
$\langle 521 321 \rangle = -\frac{675\sqrt{21}}{1605632}$	$\langle 511 431 \rangle = -\frac{6400\sqrt{3}}{301327047}$	$\langle 511 631 \rangle = -\frac{43129600\sqrt{3}}{181561972207}$	$\langle 520 600 \rangle = \frac{3258720\sqrt{21}}{181561972207}$
$\langle 522 322 \rangle = \frac{675\sqrt{21}}{802816}$	$\langle 520 300 \rangle = \frac{45\sqrt{23}}{229376}$	$\langle 520 400 \rangle = \frac{301327047}{301327047}$	$\langle 520 620 \rangle = \frac{98092800\sqrt{6}}{25937424601}$
$\langle 530 210 \rangle = -\frac{512\sqrt{5}}{823543}$	$\langle 520 320 \rangle = -\frac{675\sqrt{21}}{802816}$	$\langle 520 420 \rangle = -\frac{5081600\sqrt{14}}{2109289329}$	$\langle 520 640 \rangle = -\frac{54720000\sqrt{2}}{181561972207}$
$\langle 531 211 \rangle = -\frac{512\sqrt{30}}{2470629}$	$\langle 521 621 \rangle = \frac{49046400\sqrt{6}}{25937424601}$	$\langle 521 721 \rangle = \frac{1008175\sqrt{6}}{1088391168}$	$\langle 530 710 \rangle = \frac{637\sqrt{70}}{161243136}$
$\langle 532 652 \rangle = -\frac{23040000\sqrt{10}}{285311670611}$	$\langle 521 641 \rangle = -\frac{18240000\sqrt{15}}{181561972207}$	$\langle 521 741 \rangle = -\frac{30625\sqrt{330}}{3990767616}$	$\langle 530 730 \rangle = \frac{145775\sqrt{15}}{408146688}$
$\langle 533 433 \rangle = \frac{903981141}{903981141}$	$\langle 522 622 \rangle = -\frac{98092800\sqrt{6}}{25937424601}$	$\langle 522 722 \rangle = -\frac{1008175\sqrt{6}}{544195584}$	$\langle 530 750 \rangle = \frac{153125\sqrt{210}}{71833817088}$
$\langle 540 320 \rangle = -\frac{135\sqrt{105}}{1605632}$	$\langle 522 642 \rangle = -\frac{9120000\sqrt{30}}{181561972207}$	$\langle 522 742 \rangle = -\frac{30625\sqrt{165}}{3990767616}$	$\langle 531 711 \rangle = \frac{637\sqrt{105}}{241864704}$
$\langle 541 321 \rangle = -\frac{675\sqrt{14}}{3211264}$	$\langle 530 410 \rangle = \frac{20480\sqrt{2}}{33480783}$	$\langle 530 610 \rangle = \frac{2695680\sqrt{7}}{181561972207}$	$\langle 531 731 \rangle = \frac{145775\sqrt{15}}{544195584}$
$\langle 542 322 \rangle = -\frac{675\sqrt{7}}{3211264}$	$\langle 530 430 \rangle = -\frac{1638400\sqrt{2}}{903981141}$	$\langle 530 630 \rangle = \frac{372940800\sqrt{2}}{181561972207}$	$\langle 531 751 \rangle = \frac{153125\sqrt{21}}{23944605696}$
$\langle 543 643 \rangle = -\frac{34560000\sqrt{10}}{285311670611}$	$\langle 531 411 \rangle = \frac{40960\sqrt{3}}{100442349}$	$\langle 530 650 \rangle = -\frac{76800000\sqrt{70}}{1997181694277}$	
$\langle 544 644 \rangle = -\frac{138240000\sqrt{10}}{285311670611}$	$\langle 531 431 \rangle = -\frac{409600\sqrt{2}}{301327047}$	$\langle 531 611 \rangle = \frac{898560\sqrt{42}}{181561972207}$	
	$\langle 533 733 \rangle = -\frac{728875\sqrt{15}}{1632586752}$	$\langle 531 631 \rangle = \frac{279705600\sqrt{2}}{181561972207}$	
	$\langle 533 753 \rangle = \frac{214375\sqrt{30}}{71833817088}$	$\langle 531 651 \rangle = -\frac{230400000\sqrt{7}}{1997181694277}$	
	$\langle 540 620 \rangle = \frac{552960\sqrt{30}}{181561972207}$	$\langle 540 720 \rangle = \frac{1715\sqrt{30}}{725594112}$	
	$\langle 540 640 \rangle = \frac{691200000\sqrt{10}}{1997181694277}$	$\langle 540 740 \rangle = \frac{1071875\sqrt{55}}{16461916416}$	
	$\langle 541 621 \rangle = \frac{2764800}{181561972207}$	$\langle 540 760 \rangle = \frac{37515625\sqrt{330}}{2282719076352}$	
	$\langle 541 641 \rangle = \frac{587520000\sqrt{10}}{1997181694277}$	$\langle 541 721 \rangle = \frac{8575}{725594112}$	
	$\langle 542 422 \rangle = \frac{409600\sqrt{42}}{6327867987}$	$\langle 541 741 \rangle = \frac{3644375\sqrt{55}}{65847665664}$	
	$\langle 542 642 \rangle = \frac{1382400\sqrt{2}}{181561972207}$	$\langle 541 761 \rangle = \frac{37515625\sqrt{77}}{1141359538176}$	
	$\langle 543 743 \rangle = -\frac{1500625\sqrt{55}}{65847665664}$	$\langle 542 722 \rangle = \frac{8575\sqrt{2}}{1451188224}$	
	$\langle 543 763 \rangle = \frac{7503125\sqrt{110}}{380453179392}$	$\langle 542 742 \rangle = \frac{214375\sqrt{55}}{8230958208}$	
	$\langle 544 744 \rangle = -\frac{1500625\sqrt{55}}{16461916416}$	$\langle 542 762 \rangle = \frac{7503125\sqrt{385}}{570679769088}$	
	$\langle 544 764 \rangle = \frac{37515625\sqrt{66}}{2282719076352}$		

$\langle 600 320 \rangle > = -\frac{32}{295245}$	$\langle 600 420 \rangle > = -\frac{414\sqrt{6}}{9765625}$	$\langle 600 720 \rangle > = -\frac{12194800992\sqrt{14}}{116490425612405}$	$\langle 610 710 \rangle > = \frac{12213784164288\sqrt{10}}{582452128062025}$
$\langle 610 210 \rangle > = -\frac{201\sqrt{35}}{89600}$	$\langle 610 310 \rangle > = -\frac{35648\sqrt{35}}{10333575}$	$\langle 610 510 \rangle > = -\frac{4537728960\sqrt{7}}{181561972207}$	$\langle 610 730 \rangle > = -\frac{17995074048\sqrt{105}}{582452128062025}$
$\langle 611 211 \rangle > = \frac{201\sqrt{35}}{179200}$	$\langle 611 311 \rangle > = \frac{17824\sqrt{35}}{10333575}$	$\langle 610 630 \rangle > = -\frac{2695680\sqrt{7}}{181561972207}$	$\langle 611 711 \rangle > = -\frac{6106892082144\sqrt{10}}{582452128062025}$
$\langle 620 100 \rangle > = -\frac{5744\sqrt{21}}{12383145}$	$\langle 620 200 \rangle > = \frac{29\sqrt{21}}{215040}$	$\langle 611 511 \rangle > = \frac{2268864480\sqrt{7}}{181561972207}$	$\langle 611 731 \rangle > = -\frac{17995074048\sqrt{105}}{582452128062025}$
$\langle 621 321 \rangle > = -\frac{4736\sqrt{14}}{14467005}$	$\langle 621 421 \rangle > = -\frac{45504\sqrt{21}}{95703125}$	$\langle 611 631 \rangle > = -\frac{898560\sqrt{42}}{181561972207}$	$\langle 620 500 \rangle > = \frac{33826640\sqrt{105}}{344685916621}$
$\langle 622 322 \rangle > = \frac{9472\sqrt{14}}{14467005}$	$\langle 622 422 \rangle > = \frac{91008\sqrt{21}}{95703125}$	$\langle 620 400 \rangle > = \frac{6368\sqrt{21}}{41015625}$	$\langle 620 720 \rangle > = -\frac{98092800\sqrt{6}}{25937424601}$
$\langle 630 210 \rangle > = -\frac{123\sqrt{10}}{388400}$	$\langle 630 310 \rangle > = \frac{128\sqrt{10}}{3444525}$	$\langle 620 420 \rangle > = -\frac{91008\sqrt{21}}{95703125}$	$\langle 620 740 \rangle > = -\frac{44094468096\sqrt{66}}{1281394681736455}$
$\langle 631 211 \rangle > = -\frac{41\sqrt{15}}{179200}$	$\langle 631 311 \rangle > = \frac{256\sqrt{15}}{10333575}$	$\langle 630 510 \rangle > = \frac{64694400\sqrt{27}}{181561972207}$	$\langle 630 710 \rangle > = \frac{3040778496\sqrt{35}}{582452128062025}$
$\langle 632 752 \rangle > = -\frac{62817140736\sqrt{15}}{1281394681736455}$	$\langle 633 433 \rangle > = \frac{19968}{13671875}$	$\langle 630 630 \rangle > = -\frac{372940800\sqrt{2}}{181561972207}$	$\langle 630 730 \rangle > = \frac{322034786304\sqrt{30}}{582452128062025}$
$\langle 633 433 \rangle > = \frac{19968}{13671875}$	$\langle 633 533 \rangle > = \frac{466176000\sqrt{2}}{181561972207}$	$\langle 631 511 \rangle > = \frac{43129600\sqrt{3}}{181561972207}$	$\langle 630 750 \rangle > = -\frac{5982584832\sqrt{105}}{256278936347291}$
$\langle 640 320 \rangle > = -\frac{512\sqrt{42}}{4822335}$	$\langle 640 420 \rangle > = \frac{9216\sqrt{7}}{478515625}$	$\langle 631 631 \rangle > = \frac{101359832\sqrt{210}}{582452128062025}$	$\langle 631 711 \rangle > = \frac{582452128062025}{582452128062025}$
$\langle 641 321 \rangle > = -\frac{512\sqrt{35}}{4822335}$	$\langle 641 421 \rangle > = \frac{1536\sqrt{210}}{478515625}$	$\langle 631 731 \rangle > = \frac{241526089728\sqrt{30}}{582452128062025}$	$\langle 631 751 \rangle > = -\frac{8973877248\sqrt{42}}{256278936347291}$
$\langle 642 322 \rangle > = -\frac{256\sqrt{70}}{4822335}$	$\langle 642 422 \rangle > = \frac{1536\sqrt{105}}{478515625}$	$\langle 640 760 \rangle > = -\frac{1147095613440\sqrt{73}}{36647887897662613}$	
$\langle 643 543 \rangle > = \frac{34560000\sqrt{10}}{285311670611}$	$\langle 643 743 \rangle > = -\frac{1340004169728\sqrt{22}}{14095341499101005}$	$\langle 641 721 \rangle > = \frac{567415296\sqrt{10}}{116490425612405}$	
$\langle 644 544 \rangle > = \frac{138240000\sqrt{10}}{285311670611}$	$\langle 644 744 \rangle > = -\frac{13600016678912\sqrt{22}}{14095341499101005}$	$\langle 641 741 \rangle > = \frac{3254295840768\sqrt{22}}{14095341499101005}$	
$\langle 650 430 \rangle > = -\frac{12288\sqrt{35}}{150390625}$	$\langle 650 530 \rangle > = \frac{7680000\sqrt{70}}{1997181694277}$	$\langle 641 761 \rangle > = -\frac{229419122688\sqrt{770}}{36647887897662613}$	
$\langle 651 431 \rangle > = -\frac{18482\sqrt{14}}{150390625}$	$\langle 651 531 \rangle > = \frac{23040000\sqrt{7}}{1997181694277}$	$\langle 642 722 \rangle > = \frac{567415296\sqrt{5}}{116490425612405}$	
$\langle 652 432 \rangle > = -\frac{18432\sqrt{5}}{107421875}$	$\langle 652 532 \rangle > = \frac{23040000\sqrt{10}}{285311670611}$	$\langle 642 742 \rangle > = \frac{153143336832\sqrt{22}}{14095341499101005}$	
		$\langle 642 762 \rangle > = -\frac{458838245376\sqrt{154}}{36647887897662613}$	
		$\langle 650 730 \rangle > = \frac{295034880\sqrt{42}}{256278936347291}$	
		$\langle 650 750 \rangle > = \frac{107062252544\sqrt{3}}{3331626172514783}$	
		$\langle 651 731 \rangle > = \frac{17702028\sqrt{105}}{256278936347291}$	
		$\langle 651 751 \rangle > = -\frac{4817801576448\sqrt{3}}{16658130862573915}$	
		$\langle 652 732 \rangle > = \frac{619573248\sqrt{6}}{256278936347291}$	
		$\langle 652 752 \rangle > = \frac{321186717632\sqrt{2}}{16658130862573915}$	

$n = 6$ continued ...

$$\begin{aligned} < 653|433 > = -\frac{12288\sqrt{6}}{107421876} &< 653|533 > = \frac{18360000\sqrt{10}}{28531670611} < 653|733 > = \frac{-413048832\sqrt{6}}{266278936347291} \\ < 654|754 > = -\frac{3211867717632\sqrt{3}}{16658130862573915} &< 653|753 > = \frac{535311286272\sqrt{3}}{16658130862573915} \\ < 655|755 > = -\frac{1605933858816\sqrt{3}}{3331626172514783} \end{aligned}$$

$n = 7$

$\langle 700 320 \rangle = -\frac{392\sqrt{42}}{29296875}$	$\langle 700 520 \rangle = -\frac{18865\sqrt{2}}{362797056}$	$\langle 700 620 \rangle = -\frac{11441201296\sqrt{3}}{349471276837215}$	$\langle 710 610 \rangle = -\frac{12213784164288\sqrt{10}}{582452128062025}$
$\langle 710 210 \rangle = -\frac{2926784\sqrt{14}}{1076168025}$	$\langle 710 410 \rangle = -\frac{20835775744\sqrt{35}}{5835920535225}$	$\langle 710 510 \rangle = -\frac{708547\sqrt{70}}{1811398528}$	$\langle 710 630 \rangle = -\frac{3040778496\sqrt{35}}{582452128062025}$
$\langle 711 211 \rangle = \frac{1463392\sqrt{14}}{1076168025}$	$\langle 711 411 \rangle = \frac{10417887872\sqrt{35}}{5835920535225}$	$\langle 711 511 \rangle = \frac{708547\sqrt{70}}{362797056}$	$\langle 711 611 \rangle = \frac{6106892082144\sqrt{10}}{582452128062025}$
$\langle 720 100 \rangle = -\frac{3299\sqrt{21}}{8847360}$	$\langle 720 300 \rangle = \frac{1809\sqrt{7}}{7812500}$	$\langle 720 400 \rangle = \frac{388039424\sqrt{21}}{3501552321135}$	$\langle 720 500 \rangle = \frac{91685\sqrt{105}}{2176782336}$
$\langle 721 321 \rangle = -\frac{7371\sqrt{14}}{31250000}$	$\langle 721 521 \rangle = -\frac{1078171136\sqrt{21}}{3501552321135}$	$\langle 721 621 \rangle = -\frac{545774374656}{116490425612405}$	$\langle 720 620 \rangle = -\frac{12194800992\sqrt{14}}{116490425612405}$
$\langle 722 322 \rangle = \frac{7371\sqrt{14}}{13625000}$	$\langle 722 422 \rangle = \frac{2156342272\sqrt{21}}{3501552321135}$	$\langle 722 522 \rangle = \frac{567415296\sqrt{10}}{116490425612405}$	$\langle 720 640 \rangle = -\frac{1091548749312}{116490425612405}$
$\langle 730 210 \rangle = -\frac{541184\sqrt{2}}{1076168025}$	$\langle 730 310 \rangle = \frac{567\sqrt{3}}{39062500}$	$\langle 730 410 \rangle = \frac{1091548749312}{344195984}$	$\langle 730 510 \rangle = \frac{17995074048\sqrt{105}}{582452128062025}$
$\langle 731 211 \rangle = -\frac{561184\sqrt{2}}{1076168025}$	$\langle 731 311 \rangle = \frac{567\sqrt{3}}{39062500}$	$\langle 731 411 \rangle = \frac{1091548749312}{1945306845075}$	$\langle 730 630 \rangle = -\frac{322034786304\sqrt{30}}{582452128062025}$
$\langle 732 652 \rangle = -\frac{619573248\sqrt{6}}{256278936347291}$	$\langle 733 433 \rangle = \frac{728875\sqrt{15}}{1632586752}$	$\langle 733 533 \rangle = -\frac{1758969856\sqrt{30}}{17507761605675}$	$\langle 730 650 \rangle = -\frac{295034880\sqrt{42}}{256278936347291}$
$\langle 740 320 \rangle = -\frac{7749\sqrt{231}}{214843750}$	$\langle 740 420 \rangle = -\frac{23166976\sqrt{154}}{4279675059165}$	$\langle 740 520 \rangle = \frac{30625\sqrt{11}}{665127936}$	$\langle 731 611 \rangle = \frac{17995074048\sqrt{70}}{582452128062025}$
$\langle 741 321 \rangle = -\frac{7749\sqrt{70}}{429687500}$	$\langle 741 421 \rangle = -\frac{23166976\sqrt{155}}{12839025177495}$	$\langle 741 521 \rangle = \frac{30625\sqrt{330}}{3990767616}$	$\langle 731 631 \rangle = -\frac{241526089728\sqrt{30}}{582452128062025}$
$\langle 742 322 \rangle = -\frac{7749\sqrt{385}}{429687500}$	$\langle 742 422 \rangle = -\frac{115832488\sqrt{2310}}{12839025177495}$	$\langle 741 621 \rangle = -\frac{3644375\sqrt{55}}{65847665664}$	$\langle 731 651 \rangle = -\frac{177020928\sqrt{105}}{256278936347291}$
$\langle 743 543 \rangle = \frac{1500625\sqrt{55}}{65847665664}$	$\langle 743 643 \rangle = \frac{1340004169728\sqrt{22}}{140955341499101005}$	$\langle 741 641 \rangle = -\frac{3254295840768\sqrt{22}}{140955341499101005}$	
$\langle 744 544 \rangle = \frac{1500625\sqrt{55}}{16461916416}$	$\langle 744 644 \rangle = \frac{5360016678919\sqrt{22}}{140955341499101005}$	$\langle 742 622 \rangle = \frac{22047234048\sqrt{110}}{1281394681736455}$	
		$\langle 742 642 \rangle = \frac{15314333336832\sqrt{22}}{140955341499101005}$	

$n = 7$ continued ...

$\langle 750 430 \rangle = -\frac{873468808\sqrt{105}}{29110245319491}$	$\langle 750 530 \rangle = -\frac{153125\sqrt{210}}{71833817088}$	$\langle 750 630 \rangle = \frac{5989584832\sqrt{105}}{256278936347291}$
$\langle 751 431 \rangle = -\frac{436731904\sqrt{42}}{7703415106497}$	$\langle 751 531 \rangle = -\frac{153125\sqrt{21}}{23944605696}$	$\langle 750 650 \rangle = -\frac{1070622572544\sqrt{3}}{3331626172514783}$
$\langle 752 432 \rangle = -\frac{3057123328\sqrt{15}}{38517075532485}$	$\langle 752 532 \rangle = -\frac{214375\sqrt{30}}{47889211392}$	$\langle 751 631 \rangle = \frac{8973877248\sqrt{42}}{256278936347291}$
$\langle 753 433 \rangle = -\frac{6114246656\sqrt{15}}{115551226597455}$	$\langle 753 533 \rangle = -\frac{214375\sqrt{30}}{71833817088}$	$\langle 751 651 \rangle = -\frac{4817801576448\sqrt{3}}{10698130862573915}$
$\langle 754 654 \rangle = \frac{3211867717632\sqrt{3}}{16658130862573915}$		$\langle 752 632 \rangle = \frac{62817140736\sqrt{15}}{1281394681736455}$
$\langle 755 655 \rangle = \frac{1605933858816\sqrt{3}}{3331626172514783}$		$\langle 752 652 \rangle = -\frac{3211867717632\sqrt{3}}{16658130862573915}$
$\langle 760 540 \rangle = -\frac{37515625\sqrt{330}}{2282719076352}$	$\langle 760 640 \rangle = \frac{1147095613440\sqrt{33}}{36647887897662613}$	$\langle 753 633 \rangle = \frac{41878093824\sqrt{15}}{1281394681736455}$
$\langle 761 541 \rangle = -\frac{37515625\sqrt{77}}{1141359538176}$	$\langle 761 641 \rangle = \frac{229419122688\sqrt{770}}{36647887897662613}$	$\langle 753 653 \rangle = -\frac{535311286272\sqrt{3}}{16658130862573915}$
$\langle 762 542 \rangle = -\frac{7503125\sqrt{385}}{570679769088}$	$\langle 762 642 \rangle = \frac{458838245376\sqrt{154}}{36647887897662613}$	
$\langle 763 543 \rangle = -\frac{7503125\sqrt{110}}{380453170392}$	$\langle 763 643 \rangle = \frac{1376514736128\sqrt{11}}{36647887897662613}$	
$\langle 764 544 \rangle = -\frac{37515625\sqrt{66}}{2282719076352}$	$\langle 764 644 \rangle = \frac{229419122688\sqrt{165}}{36647887897662613}$	

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, $\langle n'l'm|nlm \rangle = \langle nlm|n'l'm \rangle$