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# Smeared 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 perturbatively 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. Chandler<sup>1</sup>. 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)<sup>2</sup>, 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)<sup>3</sup> family, like the hydrogenoid atom eigenfunctions, which constitute an asymptotic limit. Slater-type orbitals (STO)<sup>4,5</sup> 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)<sup>6</sup> or Coulomb-Sturmian orbitals (CSO)<sup>7</sup>. The techniques developed for the latter<sup>8–10</sup> 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) method<sup>11</sup>. 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<sup>11,12</sup>. 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  $\rho$  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 zero<sup>th</sup>-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 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 in <sup>13</sup>, 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,

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

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.

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

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

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

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 zero<sup>th</sup> 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 distortion with respect to spherical symmetry, takes two values:  $b = 1$  close to the no distortion 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”).

$n = 1$	$l = 0$	$m = 0$	$\psi_{1,0,0} = \psi_{1,0,0}^{(0)} + \frac{\sqrt{5}}{5a\mu Z} \sum_{n'>2} \frac{1}{1-\frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{1,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{1,0,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{\sqrt{6}}{480} \psi_{3,2,0}^{(0)} + \frac{104}{28125} \psi_{4,2,0}^{(0)} + \frac{5\sqrt{14}}{6804} \psi_{5,2,0}^{(0)} + \frac{5744\sqrt{21}}{12353145} \psi_{6,2,0}^{(0)} + \frac{3299\sqrt{21}}{8847360} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 2$	$l = 0$	$m = 0$	$\psi_{2,0,0} = \psi_{2,0,0}^{(0)} + \frac{4\sqrt{5}}{5a\mu Z} \sum_{n'>2} \frac{1}{1-\frac{4}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{2,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{2,0,0}^{(0)} - \frac{\mu^2 Z^2}{a} \left( \frac{32\sqrt{3}}{9375} \psi_{3,2,0}^{(0)} + \frac{2\sqrt{2}}{1215} \psi_{4,2,0}^{(0)} + \frac{3680\sqrt{7}}{7411887} \psi_{5,2,0}^{(0)} + \frac{29\sqrt{42}}{215040} \psi_{6,2,0}^{(0)} + \frac{63584\sqrt{42}}{645700815} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 2$	$l = 1$	$m = 0$	$\psi_{2,1,0} = \psi_{2,1,0}^{(0)} + \frac{8}{5a\mu Z} \sum_{n'>2} \frac{1}{1-\frac{4}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{2,1}(r)}{r} dr \psi_{n',1,0}^{(0)} + \frac{12\sqrt{21}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{1}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{2,1}(r)}{r} dr \psi_{n',3,0}^{(0)}$ $= \psi_{2,1,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{192}{3125} \psi_{3,1,0}^{(0)} + \frac{56\sqrt{10}}{6075} \psi_{4,1,0}^{(0)} + \frac{8768\sqrt{5}}{1058841} \psi_{5,1,0}^{(0)} + \frac{201\sqrt{35}}{8960} \psi_{6,1,0}^{(0)} + \frac{2926784\sqrt{14}}{1076168025} \psi_{7,1,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{8\sqrt{10}}{14175} \psi_{4,3,0}^{(0)} + \frac{512\sqrt{5}}{823543} \psi_{5,3,0}^{(0)} + \frac{123\sqrt{10}}{358400} \psi_{6,3,0}^{(0)} + \frac{541184\sqrt{3}}{1076168025} \psi_{7,3,0}^{(0)} + \dots \right)$
$n = 2$	$l = 1$	$m = \pm 1$	$\psi_{2,1,\pm 1} = \psi_{2,1,\pm 1}^{(0)} - \frac{4}{5a\mu Z} \sum_{n'>2} \frac{1}{1-\frac{4}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{2,1}(r)}{r} dr \psi_{n',1,\pm 1}^{(0)}$ $+ \frac{12\sqrt{14}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{4}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{2,1}(r)}{r} dr \psi_{n',3,\pm 1}^{(0)}$ $= \psi_{2,1,\pm 1}^{(0)} - \frac{\mu^2 Z^2}{a} \left( \frac{96}{3125} \psi_{3,1,\pm 1}^{(0)} + \frac{28\sqrt{10}}{6075} \psi_{4,1,\pm 1}^{(0)} + \frac{4384\sqrt{5}}{1058841} \psi_{5,1,\pm 1}^{(0)} + \frac{201\sqrt{35}}{179200} \psi_{6,1,\pm 1}^{(0)} + \frac{1463392\sqrt{14}}{1076168025} \psi_{7,1,\pm 1}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{16\sqrt{15}}{42525} \psi_{4,3,\pm 1}^{(0)} + \frac{512\sqrt{30}}{2470629} \psi_{5,3,\pm 1}^{(0)} + \frac{41\sqrt{15}}{179200} \psi_{6,3,\pm 1}^{(0)} + \frac{541184\sqrt{2}}{1076168025} \psi_{7,3,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 0$	$m = 0$	$\psi_{3,0,0} = \psi_{3,0,0}^{(0)} + \frac{27\sqrt{5}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,0}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{3,0,0}^{(0)} - \frac{\mu^2 Z^2}{a} \left( \frac{792\sqrt{3}}{588245} \psi_{4,2,0}^{(0)} + \frac{45\sqrt{42}}{229376} \psi_{5,2,0}^{(0)} + \frac{656\sqrt{7}}{2066715} \psi_{6,2,0}^{(0)} + \frac{1809\sqrt{7}}{7812500} \psi_{7,2,0}^{(0)} + \dots \right)$
$n = 3$	$l = 1$	$m = 0$	$\psi_{3,1,0} = \psi_{3,1,0}^{(0)} + \frac{18}{5a\mu Z} \sum_{n'>1} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{3,1}(r)}{r} dr \psi_{n',1,0}^{(0)} + \frac{27\sqrt{21}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{3,1}(r)}{r} dr \psi_{n',3,0}^{(0)}$ $= \psi_{3,1,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{-192}{3125} \psi_{2,1,0}^{(0)} + \frac{60288\sqrt{10}}{2941225} \psi_{4,1,0}^{(0)} + \frac{231\sqrt{5}}{16384} \psi_{5,1,0}^{(0)} + \frac{35648\sqrt{35}}{10333575} \psi_{6,1,0}^{(0)} + \frac{310191\sqrt{14}}{78125000} \psi_{7,1,0}^{(0)} + \dots \right)$ $- \frac{\mu^2 Z^2}{a} \left( \frac{10368\sqrt{10}}{20588575} \psi_{4,3,0}^{(0)} + \frac{81\sqrt{5}}{458752} \psi_{5,3,0}^{(0)} + \frac{128\sqrt{10}}{3444525} \psi_{6,3,0}^{(0)} + \frac{567\sqrt{3}}{39062500} \psi_{7,3,0}^{(0)} + \dots \right)$
$n = 3$	$l = 1$	$m = \pm 1$	$\psi_{3,1,\pm 1} = \psi_{3,1,\pm 1}^{(0)} - \frac{9}{5a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',1}(r)R_{3,1}(r)}{r} dr \psi_{n',1,\pm 1}^{(0)} + \frac{27\sqrt{14}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',3}(r)R_{3,1}(r)}{r} dr \psi_{n',3,\pm 1}^{(0)}$ $= \psi_{3,1,\pm 1}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{96}{3125} \psi_{2,1,\pm 1}^{(0)} - \frac{30144\sqrt{10}}{2941225} \psi_{4,1,\pm 1}^{(0)} - \frac{231\sqrt{5}}{32768} \psi_{5,1,\pm 1}^{(0)} - \frac{17824\sqrt{35}}{10333575} \psi_{6,1,\pm 1}^{(0)} - \frac{310191\sqrt{14}}{156250000} \psi_{7,1,\pm 1}^{(0)} + \dots \right)$ $- \frac{\mu^2 Z^2}{a} \left( \frac{6912\sqrt{15}}{20588575} \psi_{4,3,\pm 1}^{(0)} + \frac{27\sqrt{5}}{458752} \psi_{5,3,\pm 1}^{(0)} + \frac{256\sqrt{15}}{10333575} \psi_{6,3,\pm 1}^{(0)} + \frac{567\sqrt{2}}{39062500} \psi_{7,3,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = 0$	$\psi_{3,2,0} = \psi_{3,2,0}^{(0)} + \frac{9\sqrt{5}}{5a\mu Z} \sum_{n'>0} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',0}(r)R_{3,2}(r)}{r} dr \psi_{n',0,0}^{(0)} + \frac{18}{7a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,0}^{(0)}$ $= \psi_{3,2,0}^{(0)} + \frac{54\sqrt{5}}{35a\mu Z} \sum_{n'>4} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,0}^{(0)}$ $= \psi_{3,2,0}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{-\sqrt{6}}{480} \psi_{1,0,0}^{(0)} + \frac{32\sqrt{3}}{9375} \psi_{2,0,0}^{(0)} + \frac{128\sqrt{6}}{1764735} \psi_{4,0,0}^{(0)} + \frac{5\sqrt{30}}{196608} \psi_{5,0,0}^{(0)} + \frac{32}{295245} \psi_{6,0,0}^{(0)} + \frac{392\sqrt{42}}{29296875} \psi_{7,0,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{13824\sqrt{6}}{4117715} \psi_{4,2,0}^{(0)} + \frac{675\sqrt{21}}{802816} \psi_{5,2,0}^{(0)} + \frac{9472\sqrt{14}}{14467005} \psi_{6,2,0}^{(0)} + \frac{7371\sqrt{14}}{15625000} \psi_{7,2,0}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{135\sqrt{105}}{1605632} \psi_{5,4,0}^{(0)} + \frac{512\sqrt{42}}{4822335} \psi_{6,4,0}^{(0)} + \frac{7749\sqrt{231}}{214843750} \psi_{7,4,0}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = \pm 1$	$\psi_{3,2,\pm 1} = \psi_{3,2,\pm 1}^{(0)} + \frac{9}{7a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,\pm 1}^{(0)} + \frac{9\sqrt{6}}{7a\mu Z} \sum_{n'>4} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,\pm 1}^{(0)}$ $= \psi_{3,2,\pm 1}^{(0)} + \frac{\mu^2 Z^2}{a} \left( \frac{6912\sqrt{6}}{4117715} \psi_{4,2,\pm 1}^{(0)} + \frac{675\sqrt{21}}{1605632} \psi_{5,2,\pm 1}^{(0)} + \frac{4736\sqrt{14}}{14467005} \psi_{6,2,\pm 1}^{(0)} + \frac{7371\sqrt{14}}{31250000} \psi_{7,2,\pm 1}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{675\sqrt{14}}{3211264} \psi_{5,4,\pm 1}^{(0)} + \frac{512\sqrt{35}}{4822335} \psi_{6,4,\pm 1}^{(0)} + \frac{7749\sqrt{770}}{429687500} \psi_{7,4,\pm 1}^{(0)} + \dots \right)$
$n = 3$	$l = 2$	$m = \pm 2$	$\psi_{3,2,\pm 2} = \psi_{3,2,\pm 2}^{(0)} - \frac{18\sqrt{5}}{35a\mu Z} \sum_{n'>3} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',2}(r)R_{3,2}(r)}{r} dr \psi_{n',2,\pm 2}^{(0)} + \frac{9\sqrt{3}}{7a\mu Z} \sum_{n'>4} \frac{1}{1-\frac{9}{n'^2}} \int_0^{+\infty} \frac{R_{n',4}(r)R_{3,2}(r)}{r} dr \psi_{n',4,\pm 2}^{(0)}$ $= \psi_{3,2,\pm 2}^{(0)} - \frac{\mu^2 Z^2}{a} \left( \frac{13824\sqrt{6}}{4117715} \psi_{4,2,\pm 2}^{(0)} + \frac{675\sqrt{21}}{802816} \psi_{5,2,\pm 2}^{(0)} + \frac{9472\sqrt{14}}{14467005} \psi_{6,2,\pm 2}^{(0)} + \frac{7371\sqrt{14}}{15625000} \psi_{7,2,\pm 2}^{(0)} + \dots \right)$ $+ \frac{\mu^2 Z^2}{a} \left( \frac{675\sqrt{7}}{3211264} \psi_{5,4,\pm 2}^{(0)} + \frac{256\sqrt{70}}{4822335} \psi_{6,4,\pm 2}^{(0)} + \frac{7749\sqrt{385}}{429687500} \psi_{7,4,\pm 2}^{(0)} + \dots \right)$

### 3 Application to EN-MFCI calculations

Although the model Hamiltonian depends upon 3 parameters,  $\mu$ ,  $Z$ , 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  $\chi_i$ '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  $\chi_i$ '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 module<sup>14</sup> that can be included in the MOLPRO quantum chemistry package<sup>15</sup> 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 Carre-

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  $\mu$  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 STOs<sup>14</sup>.

A hyperbolic cosine factor can be associated to ETO to provide a “double zeta” character to a minimal basis set<sup>16</sup>. 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, sp<sub>2</sub>, or sp<sub>3</sub> 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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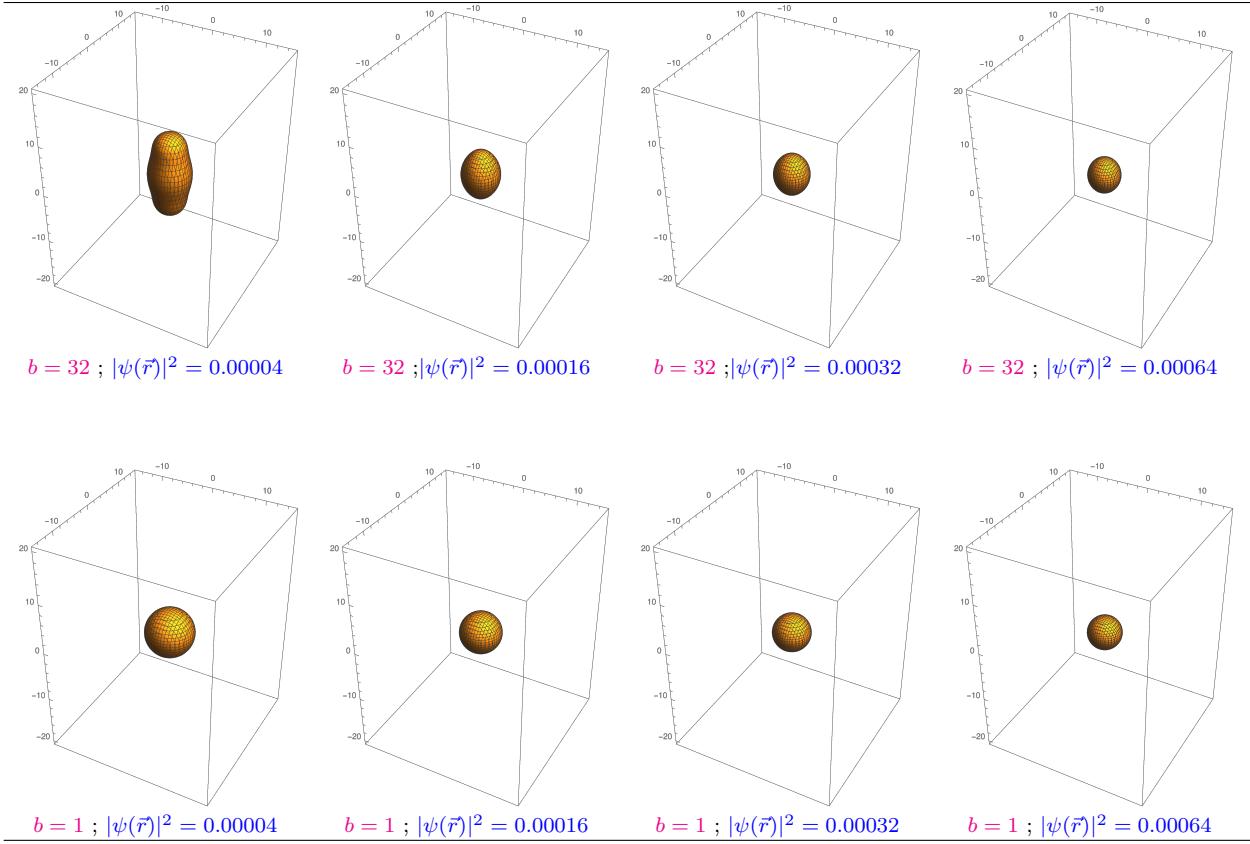


Figure 1: Comparison of hydrogen smeared Coulomb potential 1s orbital squared density levels.

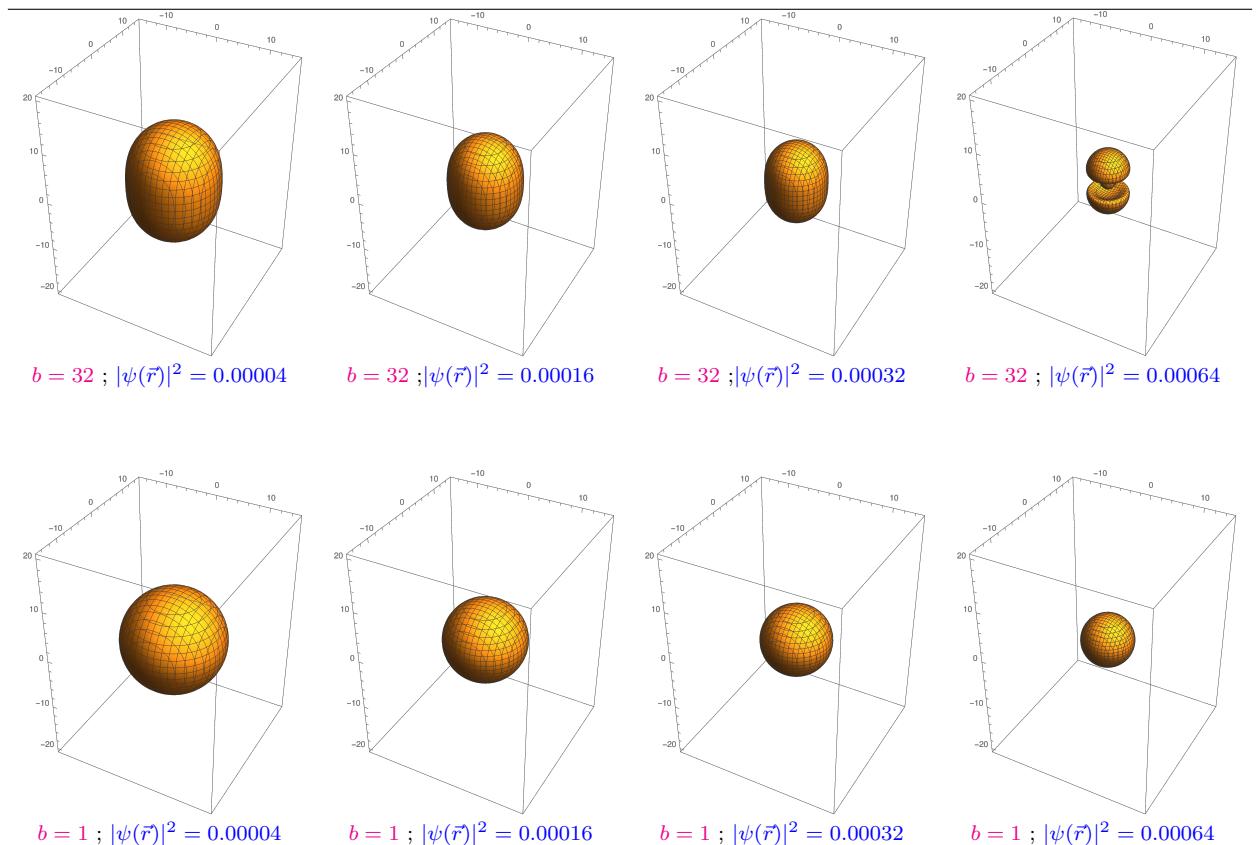


Figure 2: Comparison of hydrogen smeared Coulomb potential 2s orbital squared density levels.

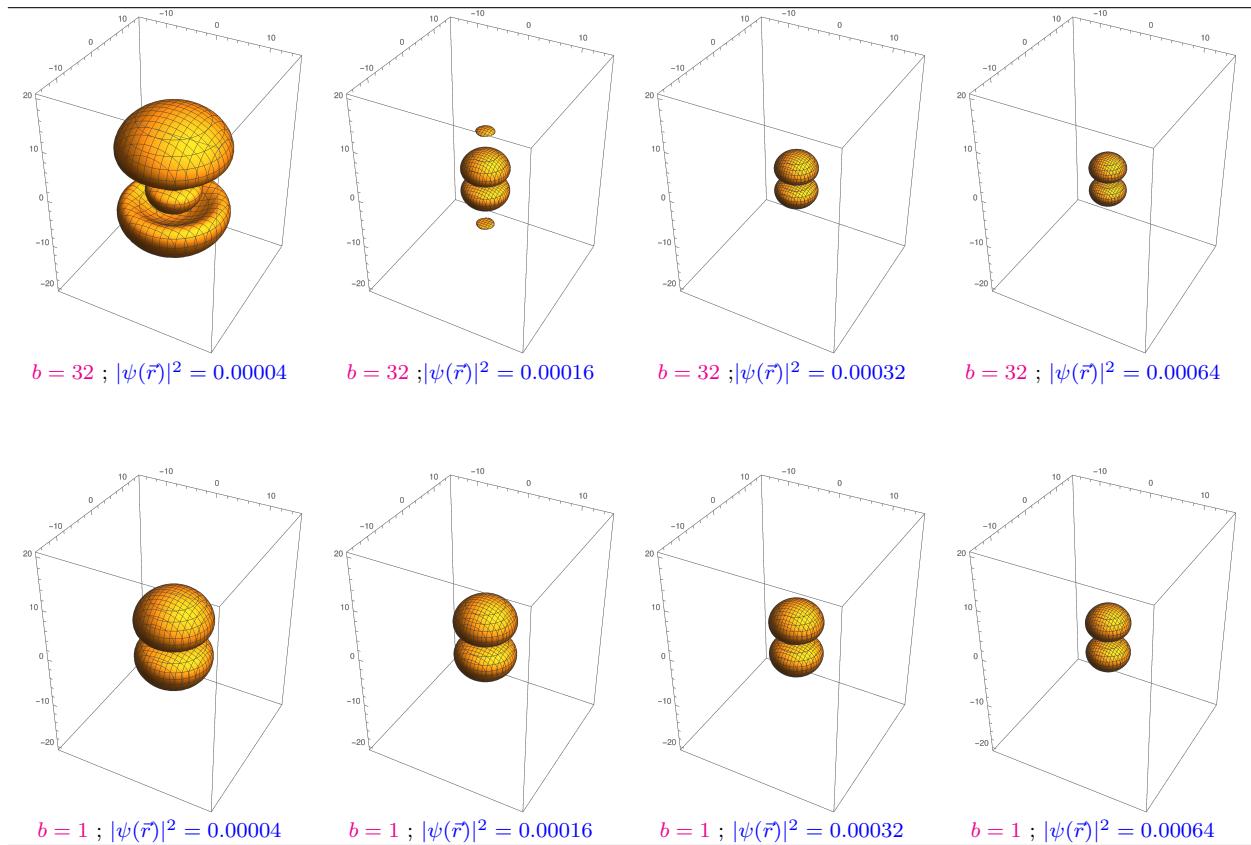


Figure 3: Comparison of hydrogen smeared Coulomb potential  $2p_z$  orbital squared density levels.

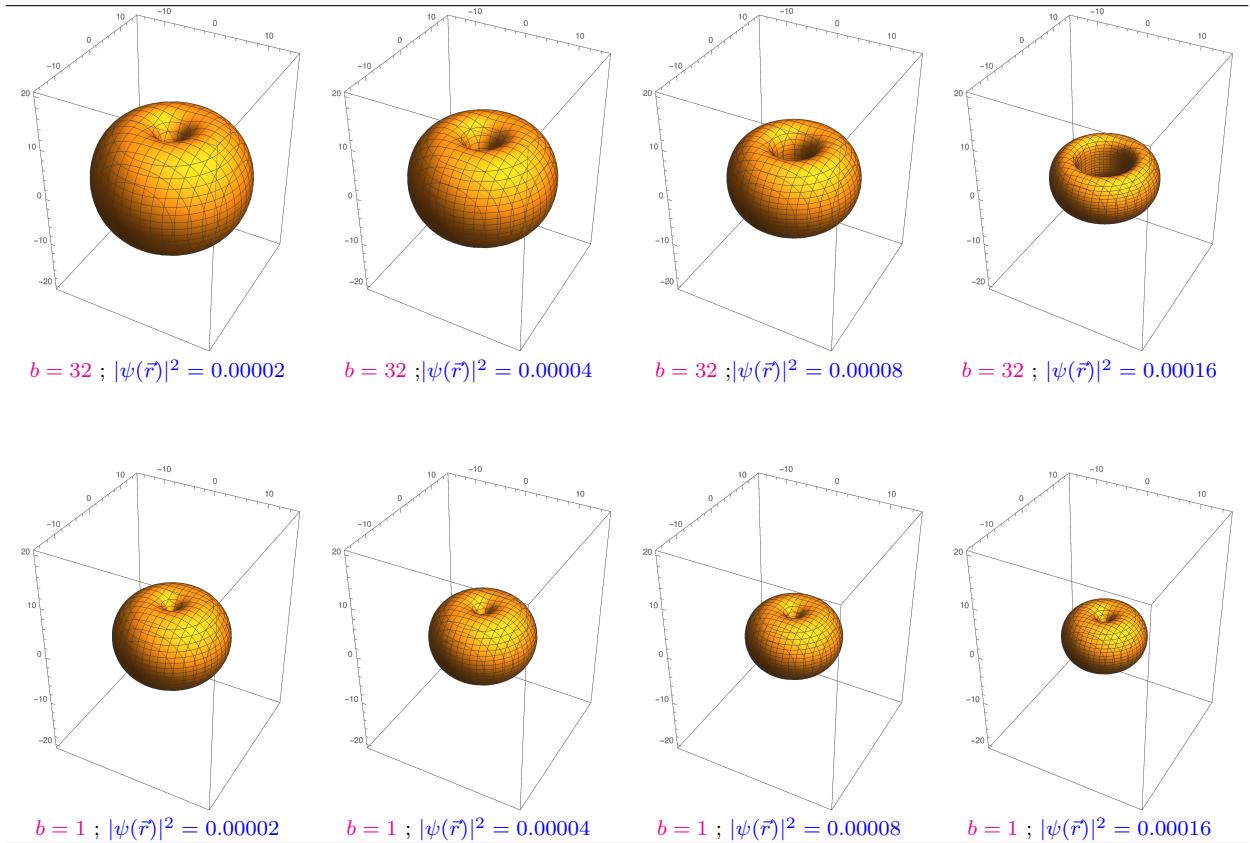


Figure 4: Comparison of hydrogen smeared Coulomb potential  $2p_{\pm 1}$  ( $m = \pm 1$ ) orbital squared density levels.

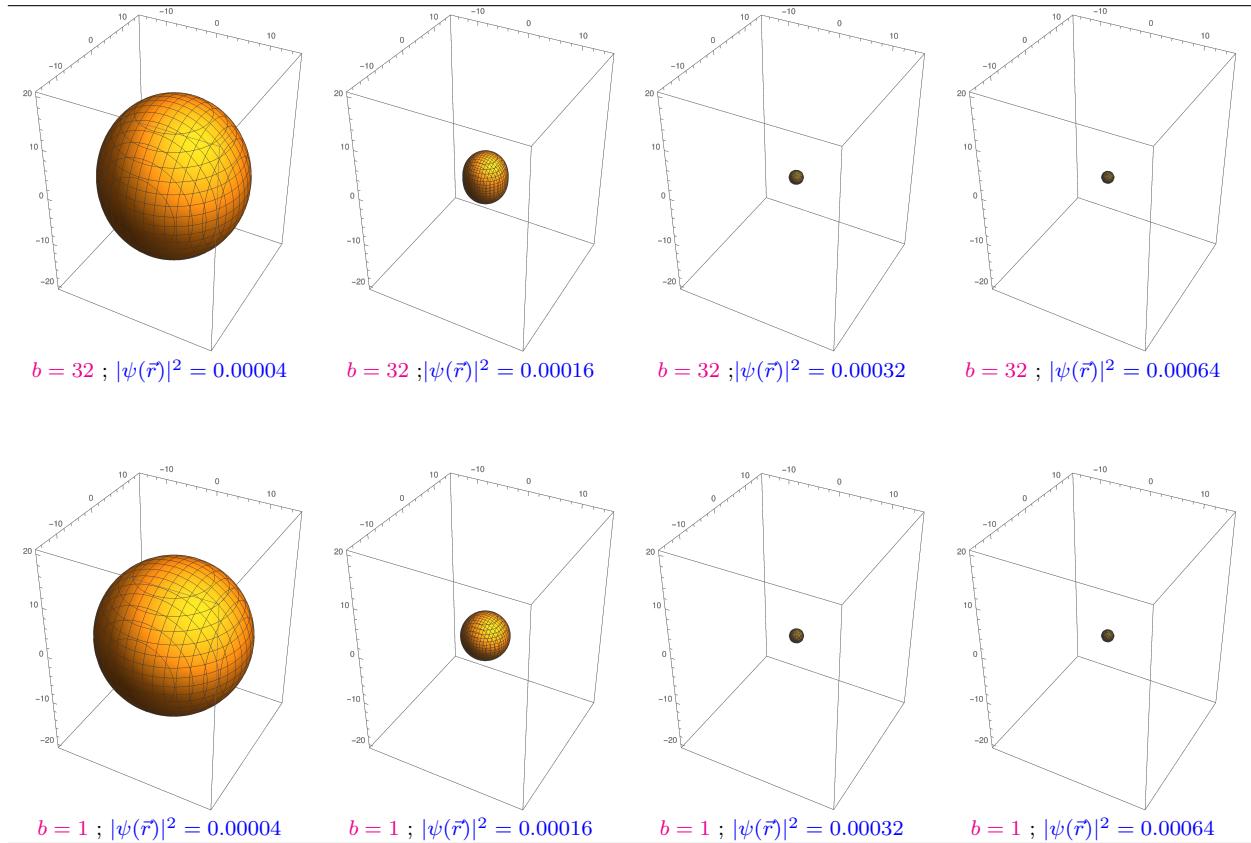


Figure 5: Comparison of hydrogen smeared Coulomb potential 3s orbital squared density levels.

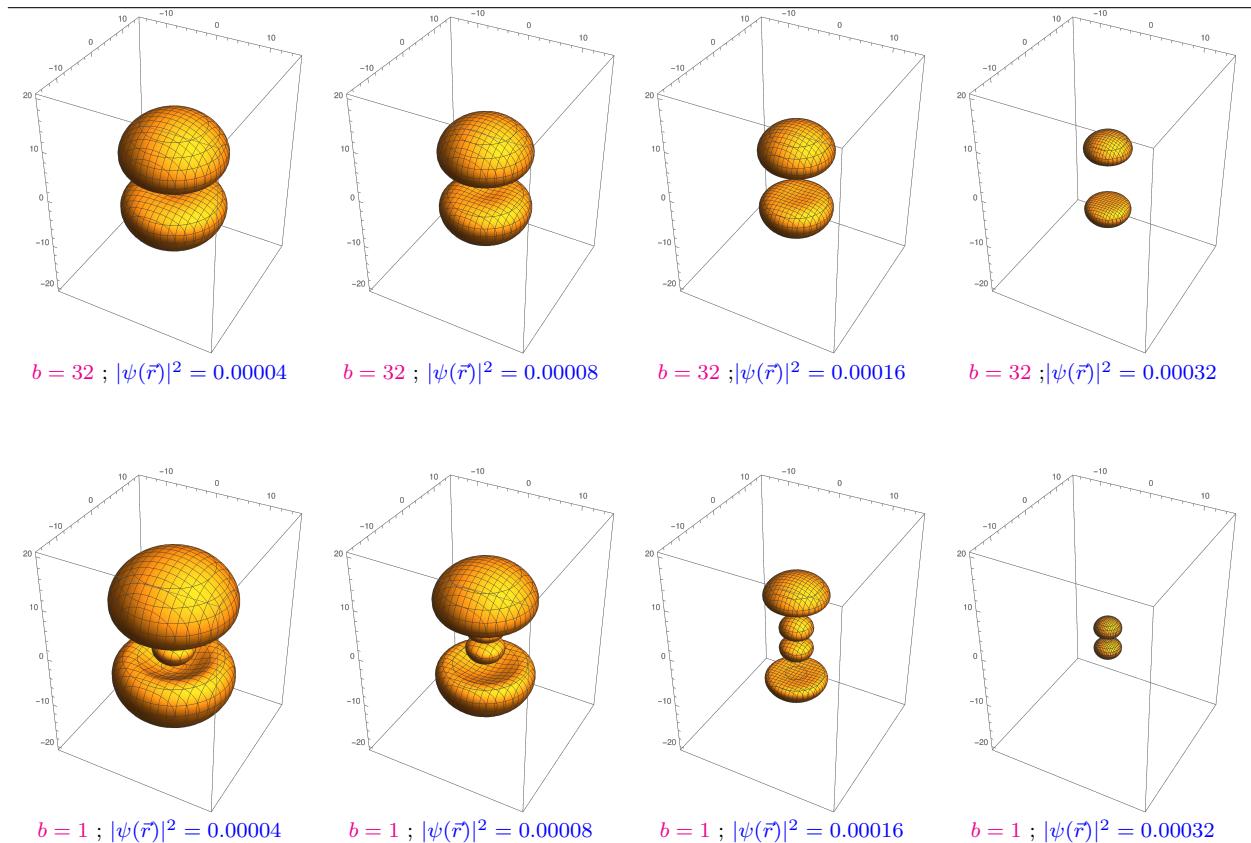


Figure 6: Comparison of hydrogen smeared Coulomb potential 3p<sub>z</sub> orbital squared density levels.

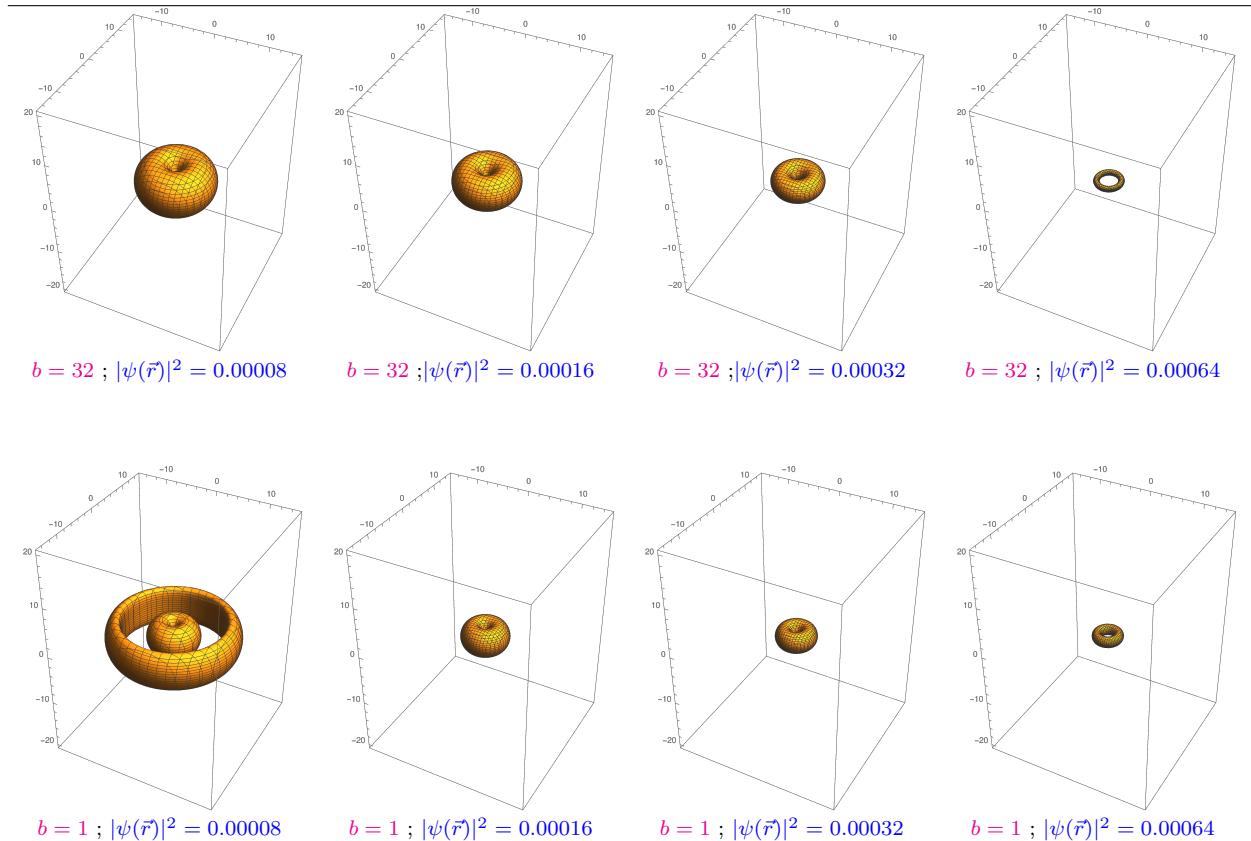


Figure 7: Comparison of hydrogen smeared Coulomb potential  $3p_{\pm 1}$  ( $m = \pm 1$ ) orbital squared density levels.

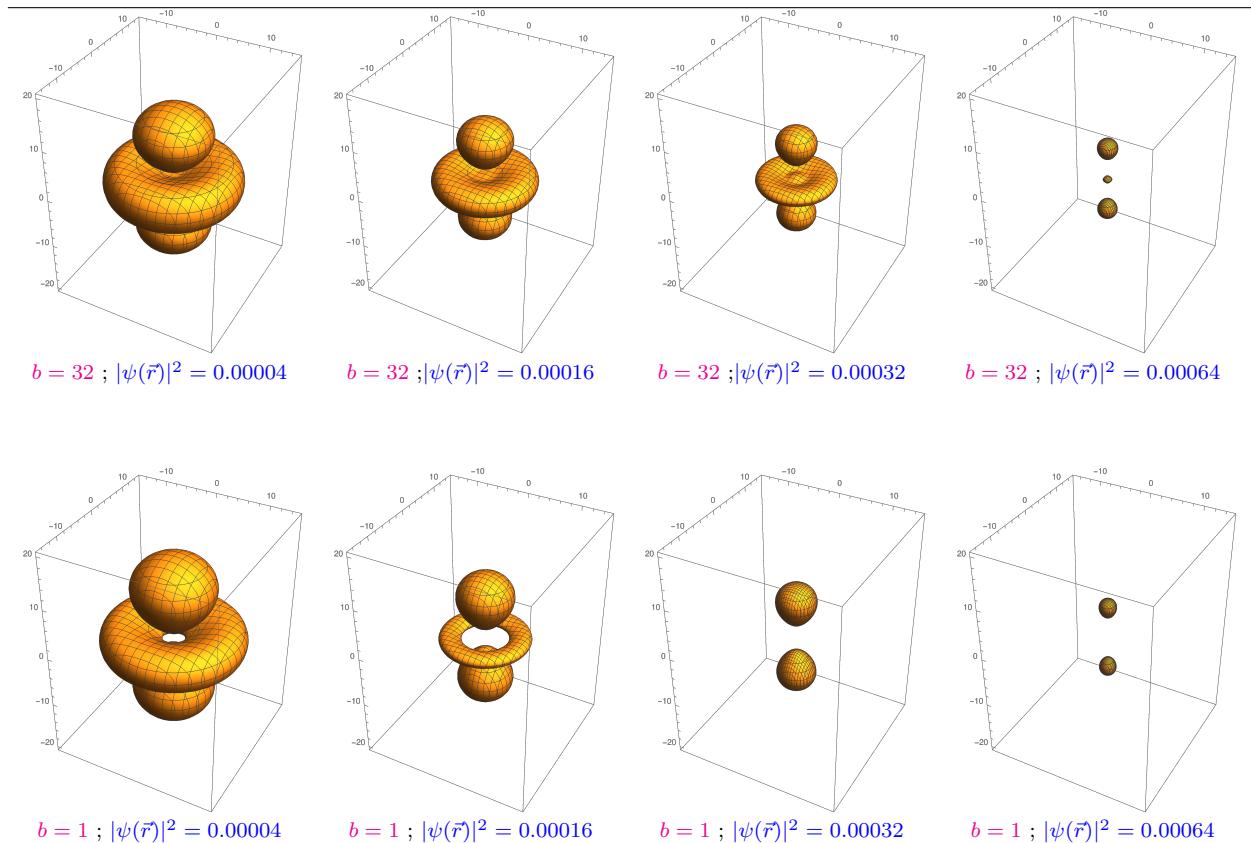


Figure 8: Comparison of hydrogen smeared Coulomb potential  $3d_{z^2}$  orbital squared density levels.

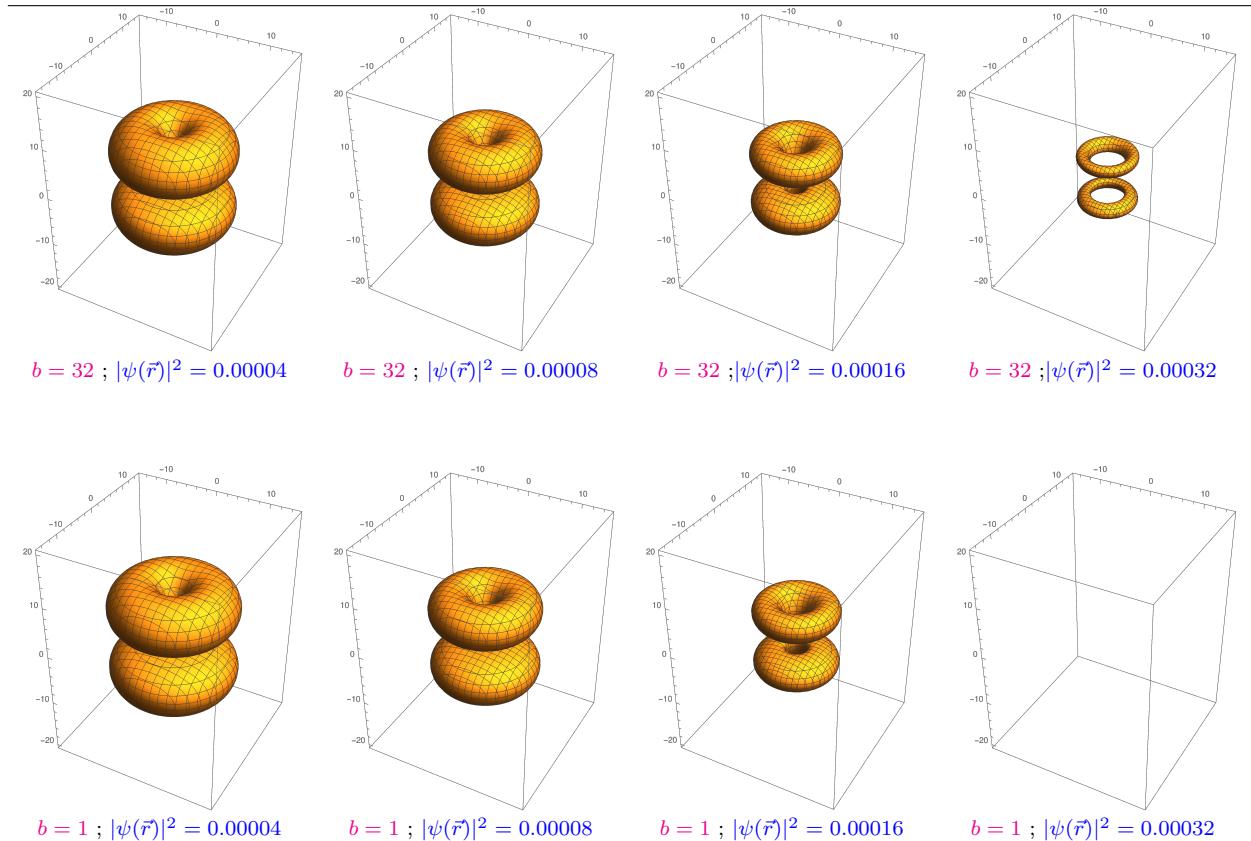


Figure 9: Comparison of hydrogen smeared Coulomb potential  $3d_{\pm 1}$  ( $m = \pm 1$ ) orbital squared density levels.

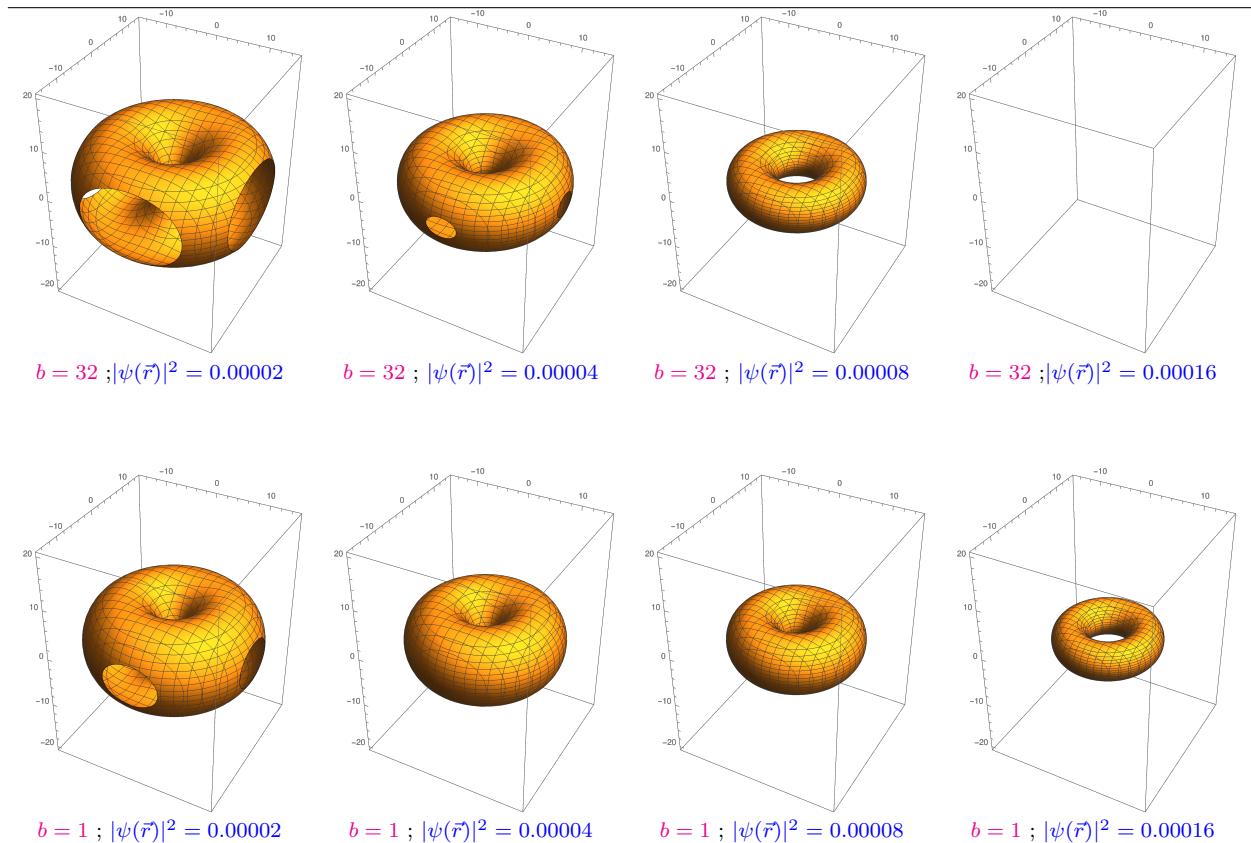


Figure 10: Comparison of hydrogen smeared Coulomb potential  $3d_{\pm 2}$  ( $m = \pm 2$ ) orbital squared density levels.

## Appendix: First order corrected eigenstates up to n=7

$n = 1$	$E_1^0 = -\frac{\mu Z^2}{2}$
$l = 0$	$E_{1,0,0}^1 = 0$

$n = 2$	$E_2^0 = -\frac{\mu Z^2}{8}$
$l = 0$	$E_{2,0,0}^1 = 0$
$l = 1$	$E_{2,1,0}^1 = -\frac{\mu^3 Z^4}{120a}$

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$n = 3$	$E_3^0 = -\frac{\mu Z^2}{18}$
$l = 0$	$E_{3,0,0}^1 = 0$
$l = 1$	$E_{3,1,0}^1 = -\frac{\mu^3 Z^4}{405a}$
$l = 2$	$E_{3,2,0}^1 = -\frac{\mu^3 Z^4}{2835a}$
$n = 4$	$E_4^0 = -\frac{\mu Z^2}{32}$
$l = 0$	$E_{4,0,0}^1 = 0$
$l = 1$	$E_{4,1,0}^1 = -\frac{\mu^3 Z^4}{960a}$
$l = 2$	$E_{4,2,0}^1 = -\frac{\mu^3 Z^4}{6720a}$
$l = 3$	$E_{4,3,0}^1 = -\frac{\mu^3 Z^4}{20160a}$

$$n = 5 \quad | \quad E_5^0 = -\frac{\mu Z^2}{50}$$

$n = 5$	$E_{5,0,0}^1 = 0$
$l = 0$	$E_{5,0,0}^1 = 0$
$l = 1$	$E_{5,1,0}^1 = -\frac{\mu^3 Z^4}{1875a}$
$l = 2$	$E_{5,2,0}^1 = -\frac{\mu^3 Z^4}{13125a}$
$l = 3$	$E_{5,3,0}^1 = -\frac{\mu^3 Z^4}{39375a}$
$l = 4$	$E_{5,4,0}^1 = -\frac{\mu^3 Z^4}{86625a}$

$n = 6$	$E_6^0 = -\frac{\mu Z^2}{72}$
$l = 0$	$E_{6,0,0}^1 = 0$
$l = 1$	$E_{6,1,0}^1 = -\frac{\mu^3 Z^4}{3240a}$
$l = 2$	$E_{6,2,0}^1 = -\frac{\mu^3 Z^4}{22680a}$
$l = 3$	$E_{6,3,0}^1 = -\frac{\mu^3 Z^4}{68040a}$
$l = 4$	$E_{6,4,0}^1 = -\frac{\mu^3 Z^4}{149688a}$
$l = 5$	$E_{6,5,0}^1 = -\frac{\mu^3 Z^4}{277992a}$

$n = 7$	$E_7^0 = -\frac{\mu Z^2}{98}$
$l = 0$	$E_{7,0,0}^1 = 0$
$l = 1$	$E_{7,1,0}^1 = -\frac{\mu^3 Z^4}{5145a}$
$l = 2$	$E_{7,2,0}^1 = -\frac{\mu^3 Z^4}{36015a}$
$l = 3$	$E_{7,3,0}^1 = -\frac{\mu^3 Z^4}{108045a}$
$l = 4$	$E_{7,4,0}^1 = -\frac{\mu^3 Z^4}{237639a}$
$l = 5$	$E_{7,5,0}^1 = -\frac{\mu^3 Z^4}{441441a}$
$l = 6$	$E_{7,6,0}^1 = -\frac{\mu^3 Z^4}{735735a}$

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

$n = 1$

$$< 100|320 >= \frac{\sqrt{6}}{480} \quad < 100|420 >= \frac{104}{28125} \quad < 100|520 >= \frac{5\sqrt{14}}{6804} \quad < 100|620 >= \frac{5744\sqrt{21}}{12553145} \quad < 100|720 >= \frac{3299\sqrt{21}}{8847360}$$

$n = 2$

$$\begin{aligned} &< 200|320 >= -\frac{32\sqrt{3}}{9375} \quad < 200|420 >= -\frac{2\sqrt{2}}{1215} \quad < 200|520 >= -\frac{3680\sqrt{7}}{7411887} \quad < 200|620 >= -\frac{29\sqrt{42}}{215040} \quad < 200|720 >= -\frac{63584\sqrt{42}}{645700815} \\ &< 210|310 >= \frac{192}{3125} \quad < 210|410 >= \frac{56\sqrt{10}}{6075} \quad < 210|510 >= \frac{8768\sqrt{5}}{1058841} \quad < 210|610 >= \frac{201\sqrt{35}}{89600} \quad < 210|710 >= \frac{2926784\sqrt{14}}{1076168025} \\ &\quad < 210|430 >= \frac{8\sqrt{10}}{14175} \quad < 210|530 >= \frac{512\sqrt{5}}{833543} \quad < 210|630 >= \frac{123\sqrt{10}}{358400} \quad < 210|730 >= \frac{541184\sqrt{3}}{1076168025} \\ &< 211|311 >= -\frac{96}{3125} \quad < 211|411 >= -\frac{28\sqrt{10}}{6075} \quad < 211|511 >= -\frac{4384\sqrt{5}}{1058841} \quad < 211|611 >= -\frac{201\sqrt{35}}{179200} \quad < 211|711 >= -\frac{1463392\sqrt{14}}{1076168025} \\ &\quad < 211|431 >= \frac{16\sqrt{15}}{42525} \quad < 211|531 >= \frac{512\sqrt{30}}{247629} \quad < 211|631 >= \frac{41\sqrt{15}}{179200} \quad < 211|731 >= \frac{541184\sqrt{2}}{1076168025} \end{aligned}$$

$n = 3$

$$\begin{aligned} &< 300|420 >= -\frac{792\sqrt{3}}{588245} \quad < 300|520 >= -\frac{45\sqrt{42}}{229376} \quad < 300|620 >= -\frac{656\sqrt{7}}{2066715} \quad < 300|720 >= -\frac{1809\sqrt{7}}{7812500} \\ &< 310|210 >= -\frac{192}{3125} \quad < 310|410 >= \frac{60288\sqrt{10}}{2941225} \quad < 310|510 >= \frac{231\sqrt{5}}{16384} \quad < 310|610 >= \frac{35648\sqrt{35}}{10333575} \quad < 310|710 >= \frac{310191\sqrt{14}}{7812500} \\ &\quad < 310|430 >= -\frac{10368\sqrt{10}}{20588575} \quad < 310|530 >= -\frac{81\sqrt{5}}{458752} \quad < 310|630 >= -\frac{128\sqrt{10}}{3444525} \quad < 310|730 >= -\frac{567\sqrt{3}}{39062500} \\ &< 311|211 >= \frac{96}{3125} \quad < 311|411 >= -\frac{30144\sqrt{10}}{2941225} \quad < 311|511 >= -\frac{231\sqrt{5}}{32768} \quad < 311|611 >= -\frac{17824\sqrt{35}}{10333575} \quad < 311|711 >= -\frac{310191\sqrt{14}}{156250000} \\ &\quad < 311|431 >= -\frac{6912\sqrt{15}}{20588575} \quad < 311|531 >= -\frac{27\sqrt{30}}{458752} \quad < 311|631 >= -\frac{256\sqrt{15}}{10333575} \quad < 311|731 >= -\frac{567\sqrt{2}}{39062500} \\ &< 320|100 >= -\frac{\sqrt{6}}{480} \quad < 320|200 >= \frac{32\sqrt{3}}{9375} \quad < 320|400 >= \frac{128\sqrt{6}}{1794735} \quad < 320|500 >= \frac{5\sqrt{30}}{166608} \quad < 320|600 >= \frac{32}{29245} \quad < 320|700 >= \frac{392\sqrt{42}}{29296875} \\ &\quad < 320|420 >= \frac{13824\sqrt{6}}{4117715} \quad < 320|520 >= \frac{675\sqrt{21}}{802816} \quad < 320|620 >= \frac{9472\sqrt{14}}{14467005} \quad < 320|720 >= \frac{7371\sqrt{14}}{15625000} \\ &\quad < 320|540 >= \frac{135\sqrt{105}}{1605632} \quad < 320|640 >= \frac{512\sqrt{42}}{4822355} \quad < 320|740 >= \frac{7749\sqrt{231}}{214843750} \\ &< 321|421 >= \frac{6912\sqrt{6}}{4117715} \quad < 321|521 >= \frac{675\sqrt{21}}{1605632} \quad < 321|621 >= \frac{4736\sqrt{14}}{14467005} \quad < 321|721 >= \frac{7371\sqrt{14}}{31250000} \\ &\quad < 321|541 >= \frac{675\sqrt{14}}{3211264} \quad < 321|641 >= \frac{512\sqrt{35}}{4822355} \quad < 321|741 >= \frac{7479\sqrt{770}}{429687500} \\ &< 322|422 >= -\frac{13824\sqrt{6}}{4117715} \quad < 322|522 >= -\frac{675\sqrt{21}}{802816} \quad < 322|622 >= -\frac{9472\sqrt{14}}{14467005} \quad < 322|722 >= -\frac{7371\sqrt{14}}{15625000} \\ &\quad < 322|542 >= \frac{675\sqrt{6}}{3211264} \quad < 322|642 >= \frac{256\sqrt{70}}{4822355} \quad < 322|742 >= \frac{7479\sqrt{385}}{429687500} \end{aligned}$$

$$n = 4$$

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$< 400 320 > = - \frac{128\sqrt{6}}{1764735}$ $< 410 210 > = - \frac{56\sqrt{10}}{6075}$ $< 411 211 > = \frac{28\sqrt{10}}{6075}$ $< 420 100 > = - \frac{104}{28125}$ $< 421 321 > = - \frac{6912\sqrt{6}}{4117715}$ $< 422 322 > = \frac{13824\sqrt{6}}{4117715}$ $< 430 210 > = - \frac{8\sqrt{10}}{14175}$ $< 431 211 > = - \frac{16\sqrt{15}}{42325}$ $< 433 533 > = - \frac{204800\sqrt{2}}{903981141}$	$< 400 520 > = - \frac{91520\sqrt{14}}{301327047}$ $< 410 310 > = - \frac{60288\sqrt{10}}{2941225}$ $< 411 311 > = \frac{30144\sqrt{10}}{2941225}$ $< 420 200 > = \frac{2\sqrt{2}}{1215}$ $< 421 521 > = \frac{2540800\sqrt{14}}{2109289329}$ $< 422 522 > = - \frac{5081600\sqrt{14}}{2109289329}$ $< 430 310 > = \frac{10368\sqrt{10}}{20585575}$ $< 431 311 > = \frac{6912\sqrt{15}}{20585575}$ $< 433 653 > = \frac{12288\sqrt{5}}{10741875}$	$< 400 620 > = - \frac{6368\sqrt{21}}{41015625}$ $< 410 610 > = \frac{590424\sqrt{14}}{683353375}$ $< 410 630 > = - \frac{20480\sqrt{2}}{33480783}$ $< 411 611 > = - \frac{1006640\sqrt{21}}{43046721}$ $< 411 631 > = - \frac{40960\sqrt{6}}{100442349}$ $< 420 300 > = \frac{2360\sqrt{5}}{42046721}$ $< 420 500 > = \frac{5081600\sqrt{14}}{2109289329}$ $< 420 520 > = - \frac{163840\sqrt{70}}{2109289329}$ $< 421 621 > = - \frac{45504\sqrt{21}}{95703125}$ $< 421 641 > = - \frac{1536\sqrt{210}}{478515625}$ $< 422 622 > = - \frac{91008\sqrt{21}}{95703125}$ $< 422 642 > = - \frac{1536\sqrt{106}}{478515625}$ $< 430 510 > = \frac{3200\sqrt{2}}{10642349}$ $< 430 530 > = \frac{1638400\sqrt{2}}{903981141}$ $< 431 511 > = \frac{6400\sqrt{3}}{301327047}$ $< 431 531 > = \frac{409600\sqrt{2}}{301327047}$ $< 432 552 > = - \frac{3057123328\sqrt{15}}{3851107532435}$ $< 433 633 > = - \frac{19968}{13671875}$ $< 433 733 > = - \frac{175869856\sqrt{30}}{10504636963405}$
$n = 4$  $< 431 211 > = - \frac{16\sqrt{15}}{42325}$ $< 433 533 > = - \frac{204800\sqrt{2}}{903981141}$	$< 430 720 > = - \frac{388039424\sqrt{21}}{360155321135}$ $< 440 710 > = \frac{208337744\sqrt{35}}{683353375225}$ $< 440 730 > = - \frac{81342464\sqrt{30}}{1945306845075}$ $< 441 711 > = - \frac{1041788877\sqrt{35}}{3833920535225}$ $< 441 731 > = - \frac{162684928\sqrt{5}}{1945306845075}$ $< 442 700 > = - \frac{4159512\sqrt{7}}{126687123005}$ $< 442 720 > = \frac{216634222\sqrt{21}}{350155321135}$ $< 442 740 > = \frac{23166976\sqrt{154}}{4279675059165}$ $< 443 730 > = - \frac{1016064\sqrt{210}}{683353375}$ $< 443 751 > = \frac{17587761605675}{7703415106497}$	$< 400 720 > = - \frac{388039424\sqrt{21}}{360155321135}$ $< 410 710 > = \frac{208337744\sqrt{35}}{683353375225}$ $< 410 730 > = - \frac{81342464\sqrt{30}}{1945306845075}$ $< 411 711 > = - \frac{1041788877\sqrt{35}}{3833920535225}$ $< 411 731 > = - \frac{162684928\sqrt{5}}{1945306845075}$ $< 420 600 > = - \frac{414\sqrt{6}}{976525}$ $< 420 620 > = \frac{91008\sqrt{21}}{95703125}$ $< 420 640 > = - \frac{9216\sqrt{7}}{478515625}$ $< 421 721 > = \frac{1078171136\sqrt{21}}{3501552321135}$ $< 421 741 > = \frac{23166976\sqrt{115}}{12839025177495}$ $< 422 722 > = - \frac{215634227\sqrt{21}}{3501552321135}$ $< 422 742 > = \frac{1158348\sqrt{2310}}{12839025177495}$ $< 430 610 > = \frac{648\sqrt{14}}{783539375}$ $< 430 630 > = \frac{79372}{783539375}$ $< 430 650 > = \frac{12288\sqrt{35}}{150390625}$ $< 431 611 > = \frac{432\sqrt{21}}{783539375}$ $< 431 631 > = \frac{59904}{783539375}$ $< 431 651 > = \frac{8432\sqrt{14}}{150390625}$ $< 430 730 > = \frac{873463808\sqrt{105}}{23101245319491}$ $< 431 731 > = \frac{1016064\sqrt{210}}{683353375}$ $< 431 751 > = \frac{17587761605675}{7703415106497}$

$n = 5$

$< 500 320 > = - \frac{5\sqrt{30}}{196608}$	$< 500 420 > = - \frac{2360\sqrt{5}}{43046721}$	$< 500 620 > = - \frac{33826640\sqrt{105}}{544685166521}$	$< 500 720 > = - \frac{91685\sqrt{105}}{2176782336}$
$< 510 210 > = - \frac{8768\sqrt{5}}{1058841}$	$< 510 310 > = - \frac{231\sqrt{5}}{16384}$	$< 510 410 > = - \frac{43046721\sqrt{2}}{43046721}$	$< 510 610 > = \frac{4537728960\sqrt{7}}{181561972207} < 510 710 > = \frac{708547\sqrt{70}}{181398528}$
$< 511 211 > = 1058841$	$< 511 311 > = \frac{231\sqrt{5}}{32768}$	$< 510 430 > = - \frac{3200\sqrt{2}}{100442349}$	$< 510 630 > = - \frac{64694400\sqrt{2}}{181561972207} < 510 730 > = - \frac{40310784}{181398528}$
$< 520 100 > = - \frac{5\sqrt{14}}{6804}$	$< 520 200 > = \frac{3680\sqrt{7}}{7411887}$	$< 511 411 > = \frac{1000640\sqrt{2}}{43046721}$	$< 511 611 > = - \frac{2268864480\sqrt{7}}{181561972207} < 511 711 > = - \frac{708547\sqrt{70}}{362797056}$
$< 521 321 > = - \frac{675\sqrt{21}}{1603632}$	$< 521 421 > = - \frac{2540800\sqrt{14}}{2109289329}$	$< 511 431 > = - \frac{6400\sqrt{3}}{301327047}$	$< 511 631 > = - \frac{181561972207\sqrt{3}}{181561972207} < 511 731 > = - \frac{2975\sqrt{10}}{40310784}$
$< 522 322 > = \frac{675\sqrt{21}}{802816}$	$< 522 422 > = \frac{5081600\sqrt{14}}{2109289329}$	$< 520 300 > = \frac{45\sqrt{42}}{229376}$	$< 520 400 > = \frac{91520\sqrt{14}}{301327047} < 520 600 > = \frac{3258720\sqrt{21}}{181561972207} < 520 700 > = \frac{18865\sqrt{2}}{362797056}$
$< 530 210 > = - \frac{512\sqrt{5}}{823543}$	$< 530 310 > = \frac{81\sqrt{5}}{458752}$	$< 520 320 > = - \frac{675\sqrt{21}}{802816}$	$< 520 420 > = - \frac{5081600\sqrt{14}}{2109289329} < 520 620 > = \frac{98092800\sqrt{6}}{25337424601} < 520 640 > = - \frac{54720000\sqrt{2}}{181561972207} < 520 740 > = - \frac{30625\sqrt{11}}{653127936}$
$< 531 211 > = - \frac{512\sqrt{30}}{2470629}$	$< 531 311 > = \frac{27\sqrt{30}}{458752}$	$< 521 421 > = - \frac{49046400\sqrt{5}}{25937424601}$	$< 521 621 > = - \frac{49046400\sqrt{5}}{25937424601} < 521 721 > = \frac{1008175\sqrt{6}}{108391168}$
$< 533 433 > = \frac{2048000\sqrt{2}}{903981141}$	$< 533 633 > = - \frac{466176000\sqrt{2}}{181561972207}$	$< 521 641 > = - \frac{18240000\sqrt{15}}{181561972207}$	$< 521 741 > = - \frac{30625\sqrt{30}}{3990767616} < 521 710 > = \frac{637\sqrt{70}}{161243136}$
$< 540 320 > = - \frac{135\sqrt{105}}{1605632}$	$< 540 420 > = \frac{1638400\sqrt{2}}{2109289329}$	$< 522 622 > = - \frac{98092800\sqrt{6}}{25937424601}$	$< 522 722 > = - \frac{1008175\sqrt{6}}{544195584} < 522 742 > = - \frac{30625\sqrt{165}}{9120000\sqrt{30}} < 522 710 > = \frac{637\sqrt{70}}{3990767616} < 530 710 > = \frac{637\sqrt{70}}{161243136}$
$< 541 321 > = - \frac{675\sqrt{14}}{3211264}$	$< 541 421 > = \frac{819200\sqrt{21}}{6327867987}$	$< 530 410 > = \frac{20480\sqrt{2}}{33480783}$	$< 530 610 > = \frac{2695680\sqrt{7}}{181561972207} < 530 730 > = \frac{145775\sqrt{15}}{408146688} < 530 750 > = \frac{153125\sqrt{210}}{408146688}$
$< 543 643 > = - \frac{23040000\sqrt{10}}{285311670611}$	$< 532 752 > = \frac{214375\sqrt{30}}{47589211392}$	$< 531 411 > = \frac{40960\sqrt{3}}{100442349}$	$< 531 611 > = \frac{372940800\sqrt{2}}{181561972207} < 531 731 > = \frac{637\sqrt{105}}{241864704} < 531 751 > = \frac{153125\sqrt{21}}{23944605696}$
$< 544 644 > = - \frac{138240000\sqrt{10}}{285311670611}$	$< 542 422 > = \frac{409600\sqrt{42}}{6327867987}$	$< 542 622 > = \frac{1382400\sqrt{2}}{181561972207}$	$< 542 722 > = \frac{8575\sqrt{55}}{1451188224} < 542 742 > = \frac{214375\sqrt{55}}{8230958208} < 542 762 > = \frac{7513125\sqrt{385}}{570679769088}$

$$\begin{aligned}
& < 600|320 > = - \frac{32}{295245} & < 600|420 > = - \frac{414\sqrt{6}}{9756325} & < 600|520 > = - \frac{3258720\sqrt{21}}{181561972207} & < 600|720 > = - \frac{12194800992\sqrt{14}}{116490424612405} \\
& < 610|210 > = - \frac{201\sqrt{35}}{89600} & < 610|310 > = - \frac{3648\sqrt{35}}{10333575} & < 610|410 > = - \frac{590424\sqrt{14}}{68359375} & < 610|510 > = - \frac{455778960\sqrt{7}}{181561972207} \\
& < 610|430 > = - \frac{64\sqrt{14}}{68359375} & < 611|211 > = \frac{201\sqrt{35}}{179200} & < 610|530 > = - \frac{2695680\sqrt{205}}{181561972207} & < 610|730 > = - \frac{179956704048\sqrt{105}}{582452128062025} \\
& < 611|411 > = \frac{17824\sqrt{35}}{10333575} & < 611|431 > = - \frac{205212\sqrt{14}}{68359375} & < 611|511 > = \frac{2268864480\sqrt{7}}{181561972207} & < 611|711 > = - \frac{6106892082144\sqrt{10}}{382452128062025} \\
& < 611|451 > = - \frac{432\sqrt{21}}{68359375} & < 611|531 > = - \frac{808560\sqrt{42}}{181561972207} & < 611|731 > = - \frac{17995074048\sqrt{7}}{532452128062025} \\
& < 620|100 > = - \frac{5744\sqrt{21}}{12353145} & < 620|200 > = \frac{29\sqrt{42}}{215040} & < 620|400 > = \frac{656\sqrt{7}}{2066715} & < 620|500 > = \frac{36826640\sqrt{105}}{5344655916621} \\
& < 620|320 > = - \frac{9472\sqrt{14}}{14467005} & < 620|420 > = - \frac{91008\sqrt{21}}{95703125} & < 620|520 > = - \frac{98092809\sqrt{6}}{25937424601} & < 620|720 > = \frac{169154749312}{16490424612405} \\
& & & < 620|540 > = - \frac{552960\sqrt{30}}{58151972207} & < 620|740 > = - \frac{44094468096\sqrt{66}}{12813944681736455} \\
& < 621|321 > = - \frac{4736\sqrt{14}}{14467005} & < 621|421 > = - \frac{45504\sqrt{21}}{95703125} & < 621|521 > = - \frac{49046400\sqrt{6}}{25337424601} & < 621|721 > = \frac{545774374656}{116490424612405} \\
& & & < 621|541 > = - \frac{2761800}{181561972207} & < 621|741 > = - \frac{44094468096\sqrt{55}}{1281394681736455} \\
& < 622|322 > = \frac{9472\sqrt{14}}{14467005} & < 622|422 > = \frac{91008\sqrt{21}}{95703125} & < 622|522 > = \frac{98092809\sqrt{6}}{26937424601} & < 622|722 > = - \frac{109145749312}{116490424612405} \\
& & & < 622|542 > = - \frac{2762400\sqrt{2}}{181561972207} & < 622|742 > = - \frac{22047234048\sqrt{110}}{1281394681736455} \\
& < 630|210 > = - \frac{123\sqrt{10}}{355400} & < 630|310 > = \frac{128\sqrt{10}}{344525} & < 630|410 > = \frac{27264}{68359375} & < 630|510 > = \frac{64694400\sqrt{2}}{181561972207} \\
& & & < 630|430 > = - \frac{75875}{68359375} & < 630|530 > = - \frac{375940800\sqrt{2}}{181561972207} & < 630|710 > = \frac{3040778496\sqrt{35}}{582452128062025} \\
& & & < 631|211 > = - \frac{41\sqrt{15}}{179200} & < 631|311 > = \frac{256\sqrt{15}}{10333575} & < 631|411 > = \frac{9088\sqrt{6}}{63539375} \\
& & & < 631|431 > = - \frac{59904}{68359375} & < 631|511 > = \frac{43129600\sqrt{3}}{181561972207} & < 631|711 > = \frac{1013592832\sqrt{210}}{582452128062025} \\
& & & < 632|752 > = - \frac{62817140736\sqrt{15}}{1281394681736455} & < 631|531 > = - \frac{275705600\sqrt{2}}{181561972207} & < 631|731 > = \frac{211526189728\sqrt{105}}{582452128062025} \\
& & & < 633|433 > = \frac{19968}{13671875} & < 633|533 > = \frac{466176000\sqrt{2}}{181561972207} & < 633|733 > = - \frac{80508396376\sqrt{70}}{116490424612405} \\
& & & < 633|753 > = - \frac{41878093824\sqrt{5}}{1281394681736455} & < 640|210 > = \frac{54720000\sqrt{2}}{181561972207} & < 640|720 > = \frac{1134830592\sqrt{8}}{116490425612405} \\
& & & < 640|520 > = \frac{691200000\sqrt{10}}{1997181694277} & < 640|540 > = - \frac{691200000\sqrt{10}}{1997181694277} & < 640|740 > = \frac{679166664416\sqrt{22}}{281906829920201} \\
& & & < 641|211 > = \frac{182400000\sqrt{15}}{181561972207} & < 641|521 > = \frac{182400000\sqrt{15}}{181561972207} & < 640|760 > = - \frac{1147095613440\sqrt{35}}{3664788789766213} \\
& & & < 641|541 > = - \frac{587520000\sqrt{10}}{1997181694277} & < 641|721 > = \frac{567415296\sqrt{10}}{116490425612405} \\
& & & < 642|322 > = - \frac{256\sqrt{70}}{4822335} & < 642|422 > = \frac{1536\sqrt{105}}{47857515625} & < 641|741 > = \frac{3284295840768\sqrt{22}}{14095341493101005} \\
& & & < 642|522 > = \frac{91200000\sqrt{30}}{181561972207} & < 642|542 > = - \frac{229419122688\sqrt{155}}{3664788789766213} & < 641|761 > = - \frac{229419122688\sqrt{770}}{3664788789766213} \\
& & & < 642|722 > = \frac{567415296\sqrt{5}}{116490425612405} & < 642|742 > = \frac{1531433356832\sqrt{22}}{14095341493101005} \\
& & & < 642|762 > = - \frac{458838245376\sqrt{154}}{3664788789766213} & < 642|782 > = \frac{3211867717632\sqrt{3}}{16658130862573915} \\
& & & < 643|543 > = \frac{345600000\sqrt{10}}{285311670611} & < 643|743 > = - \frac{1340004169728\sqrt{22}}{14095341493101005} \\
& & & < 643|763 > = - \frac{1376514736128\sqrt{11}}{3664788789766213} & < 650|730 > = \frac{29534880\sqrt{12}}{256275836347291} \\
& & & < 644|744 > = - \frac{53600166789110\sqrt{22}}{14095341493101005} & < 650|750 > = \frac{1070622872544\sqrt{3}}{333126172514783} \\
& & & < 644|764 > = \frac{229419122688\sqrt{155}}{3664788789766213} & < 651|731 > = \frac{4817801576448\sqrt{3}}{160530862573915} \\
& & & < 650|530 > = \frac{76800000\sqrt{70}}{1997181694277} & < 651|751 > = \frac{177020928\sqrt{105}}{256275836347291} \\
& & & < 651|531 > = \frac{230400000\sqrt{7}}{1997181694277} & < 652|732 > = \frac{6195732\sqrt{6}}{256275836347291} \\
& & & < 651|752 > = \frac{3211867717632\sqrt{3}}{16658130862573915} & 
\end{aligned}$$

*n = 6 continued ...*

$$\begin{aligned} < 653|433 > &= - \frac{12288\sqrt{5}}{107421875} & < 653|533 > &= \frac{15360000\sqrt{10}}{28531167611} & < 653|733 > &= \frac{413048832\sqrt{6}}{256278936337291} \\ &&&&& \\ < 654|754 > &= - \frac{3211867717632\sqrt{3}}{16653139867573915} & && & \\ < 655|755 > &= - \frac{160533358816\sqrt{3}}{3331626172514783} & && & \end{aligned}$$

$$n = 7$$

$< 700 320 > = - \frac{392\sqrt{42}}{29296875}$	$< 700 420 > = - \frac{4159512\sqrt{7}}{129687123005}$	$< 700 520 > = - \frac{18865\sqrt{2}}{362797055}$	$< 700 620 > = - \frac{11441201296\sqrt{3}}{349471276337215}$
$< 710 210 > = - \frac{2926784\sqrt{14}}{1076168025}$	$< 710 310 > = - \frac{310191\sqrt{14}}{75125000}$	$< 710 410 > = - \frac{20835775744\sqrt{35}}{553592053225}$	$< 710 510 > = - \frac{70847\sqrt{70}}{181398528}$
$< 711 211 > = \frac{1463392\sqrt{14}}{1076168025}$	$< 711 311 > = \frac{310191\sqrt{14}}{15625000}$	$< 710 430 > = - \frac{3048492\sqrt{35}}{645433615025}$	$< 710 530 > = - \frac{637\sqrt{70}}{1612413136}$
$< 720 100 > = - \frac{3299\sqrt{21}}{8847360}$	$< 720 200 > = \frac{63584\sqrt{42}}{645700815}$	$< 711 411 > = \frac{104117887872\sqrt{35}}{3535920535225}$	$< 711 511 > = \frac{70847\sqrt{70}}{362757056}$
$< 720 320 > = - \frac{7371\sqrt{14}}{15625000}$	$< 720 420 > = - \frac{7371\sqrt{14}}{15625000}$	$< 711 431 > = - \frac{1016064\sqrt{210}}{645433615025}$	$< 711 531 > = - \frac{637\sqrt{105}}{24184704}$
$< 721 321 > = - \frac{7371\sqrt{14}}{31250000}$	$< 721 421 > = - \frac{1078171136\sqrt{21}}{3501552321135}$	$< 721 521 > = - \frac{1068175\sqrt{6}}{1081168}$	$< 721 621 > = - \frac{545774474656}{116190425612405}$
$< 722 322 > = \frac{7371\sqrt{14}}{15625000}$	$< 722 422 > = \frac{2156342272\sqrt{21}}{3501552321135}$	$< 721 541 > = - \frac{8575}{2535941172}$	$< 721 641 > = - \frac{567411296\sqrt{10}}{116190425612405}$
$< 730 210 > = - \frac{541184\sqrt{3}}{1076168025}$	$< 730 310 > = \frac{567\sqrt{3}}{39062500}$	$< 722 522 > = \frac{544195584}{1945306845075}$	$< 722 622 > = \frac{1091548749312}{116190425612405}$
$< 731 211 > = - \frac{541184\sqrt{2}}{1076168025}$	$< 731 311 > = \frac{567\sqrt{2}}{39062500}$	$< 722 542 > = - \frac{8575\sqrt{2}}{1431188224}$	$< 722 642 > = - \frac{567415296\sqrt{5}}{116190425612405}$
$< 732 652 > = - \frac{619573248\sqrt{6}}{256278936347291}$	$< 732 753 > = - \frac{728875\sqrt{15}}{1632586752}$	$< 733 633 > = \frac{80508696576\sqrt{30}}{116490425612405}$	$< 730 650 > = - \frac{295034880\sqrt{42}}{256278936347291}$
$< 733 433 > = \frac{17558069856\sqrt{30}}{10504656953405}$	$< 734 320 > = - \frac{23166976\sqrt{154}}{4279675059165}$	$< 733 653 > = - \frac{413048832\sqrt{6}}{75277936347291}$	$< 731 611 > = \frac{17995074048\sqrt{70}}{582452128662025}$
$< 740 320 > = - \frac{7749\sqrt{231}}{214843750}$	$< 740 420 > = - \frac{23166976\sqrt{154}}{4279675059165}$	$< 740 520 > = \frac{3025\sqrt{11}}{66127936}$	$< 730 630 > = - \frac{322034786304\sqrt{30}}{582452128662025}$
$< 741 321 > = - \frac{7749\sqrt{770}}{429687500}$	$< 741 421 > = - \frac{23166976\sqrt{154}}{12839025177495}$	$< 740 540 > = - \frac{1071875\sqrt{55}}{16461916416}$	$< 731 631 > = - \frac{241526680728\sqrt{30}}{582452128662025}$
$< 742 322 > = - \frac{7749\sqrt{385}}{429687500}$	$< 742 422 > = - \frac{11553488\sqrt{2310}}{12839025177495}$	$< 741 541 > = - \frac{3644375\sqrt{55}}{65847666664}$	$< 731 651 > = - \frac{241526680728\sqrt{30}}{582452128662025}$
$< 743 543 > = \frac{1500625\sqrt{55}}{65847655674}$	$< 743 643 > = \frac{1340004169728\sqrt{22}}{14095341499101005}$	$< 742 522 > = \frac{3025\sqrt{165}}{390767616}$	$< 742 642 > = - \frac{1531333333832\sqrt{22}}{14095341499101005}$
$< 744 544 > = \frac{1500625\sqrt{55}}{16461916416}$	$< 744 644 > = \frac{536016678912\sqrt{22}}{14095341499101005}$		

*n = 7 continued ...*

$< 750 430 > = - \frac{873463898\sqrt{105}}{2310245319491}$	$< 750 530 > = - \frac{153125\sqrt{210}}{71833817088}$	$< 750 630 > = \frac{5982584832\sqrt{105}}{25627936337291}$
$< 751 431 > = - \frac{436731904\sqrt{42}}{7703415106497}$	$< 751 531 > = - \frac{153125\sqrt{210}}{23944605636}$	$< 750 650 > = - \frac{1070622572544\sqrt{3}}{3331636172514783}$
$< 752 432 > = - \frac{3057123328\sqrt{15}}{35517075532485}$	$< 752 532 > = - \frac{214375\sqrt{30}}{47889211352}$	$< 751 631 > = \frac{5978877248\sqrt{210}}{2627893634291}$
$< 753 433 > = - \frac{6114246656\sqrt{15}}{115551226597455}$	$< 753 533 > = - \frac{214375\sqrt{30}}{71833817088}$	$< 751 651 > = - \frac{4817801576448\sqrt{3}}{16658130862573915}$
$< 754 654 > = \frac{321186777632\sqrt{3}}{16658130862573915}$	$< 753 633 > = \frac{418780093824\sqrt{15}}{1291394681736155}$	$< 752 632 > = \frac{52817140736\sqrt{15}}{1291394681736155}$
$< 755 655 > = \frac{1605033958816\sqrt{3}}{3331636172314783}$	$< 753 633 > = - \frac{555311286227\sqrt{3}}{16658130862573915}$	$< 752 652 > = - \frac{3211867717632\sqrt{3}}{16658130862573915}$
$< 760 540 > = - \frac{37515625\sqrt{330}}{22827190763552}$	$< 760 640 > = \frac{1147095613440\sqrt{33}}{36647788739762613}$	$< 761 641 > = \frac{229419122688\sqrt{770}}{36647788739762613}$
$< 761 541 > = - \frac{37515625\sqrt{770}}{11413593838176}$	$< 762 642 > = \frac{158338245376\sqrt{754}}{36647788739762613}$	$< 762 642 > = \frac{158338245376\sqrt{754}}{36647788739762613}$
$< 762 542 > = - \frac{7563125\sqrt{385}}{570619769088}$	$< 763 643 > = \frac{1370514736128\sqrt{11}}{36647788739762613}$	$< 763 643 > = \frac{1370514736128\sqrt{11}}{36647788739762613}$
$< 763 543 > = - \frac{7563125\sqrt{110}}{350433179392}$	$< 764 644 > = \frac{229419122688\sqrt{165}}{36647788739762613}$	$< 764 644 > = \frac{229419122688\sqrt{165}}{36647788739762613}$

Table 5: Non-zero, first order coupling coefficients up to n=7 in  $\frac{\mu^2 Z^2}{a}$  units, that is to say,  $\psi_{n,l,m}^{(1)} = \sum_{(n',l') \neq (n,l)} < n'l'm | nlm > \frac{\mu^2 Z^2}{a} \psi_{n',l',m}^{(0)}$ .

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