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13. ABSTRACT (Maximum 200 words)

In preparation for computational work with molecular orbitals written as linear combinations of atomic orbitals, for first and second row atoms, we have developed a general procedure to parametrize linear combinations of Gaussian orbitals. We used a Gaussian transform, and a Gauss-Legendre quadrature, to express hydrogenic orbitals (with the correct long-range dependence for collisions) as contracted Gaussians, for a general case with varying effective charges.

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Atomic Orbital Basis Sets for Molecular Interactions

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ABSTRACT

We describe a general approach to the parametrization of linear combinations of Gaussian atomic orbitals, useful for atomic and molecular interactions. We use a Gaussian transform method and Gauss-Legendre quadratures to express hydrogenic atomic orbitals, with varying effective charges, in terms of Gaussian-type orbitals. This procedure provides well defined rules for calculating exponent factors and combination coefficients of the linear combinations of Gaussians in problems where nuclear distances may vary over large ranges during interactions.

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1. INTRODUCTION

Since the suggestion by Boys in 1950,[1] the use of Gaussian functions as basis sets has increased useful in theoretical chemistry calculations of electronic structure. Gaussian functions have been found very useful in the efficient calculation of multicenter electronic integrals. Gaussian basis sets have been parametrized to optimize the calculation of atomic and molecular energies, in work that has continued until very recently.[2-13] Gaussian functions also arise when one introduces the Gaussian transform of atomic orbitals (AOs). In this case, the transform integral is eventually discretized, to obtain a set of parametrized basis functions. The choice of discretization has again been guided by interest in the calculation of energies of stationary states.[2,3,14,15]

Basis sets are also needed in studies of atomic and molecular interactions, where the main concern is the calculation of probabilities of electronic transitions, excitation cross sections, and thermal rates. We have used atomic bases in recent studies, with a time-dependent description which construct molecular orbitals as combinations of AOs with time-dependent coefficients.[16]

In the case of atomic or molecular interactions, where distances and bond angles change over large values, it is important to work with AOs having the correct asymptotic behavior. This is given by radial functions which decrease exponentially with the distance from an electron to an atomic core, at a rate depending on the effective charge of the core. This behaviour is correctly given by hydrogenic atomic orbitals (HAO's). Their orbital exponents must change to reflect varying effective nuclear charges as nuclei or cores move and exponents change with time. The aim of this contribution is to provide a general way of expressing these HAO's in terms of Gaussian atomic orbitals (GAO's), with exponents and coefficients directly determined from the varying effective charges. Our criterion for choosing the Gaussian basis sets is that they should properly describe the AOs at distances from atomic cores that are important in dynamical phenomena, instead of emphasizing the energetics of stationary states.

The angular part of the basis function can be represented in terms of spherical harmonics $Y_{lm}(\theta, \varphi)$ or in terms of integer powers of the Cartesian coordinates. In this case a primitive

basis function may be written as

$$\eta(x, y, z) = x^{n_x} y^{n_y} z^{n_z} exp(-ar^2),$$ (1)

and a contracted Gaussian basis function is represented by[5]

$$\chi(x, y, z) = x^{n_x} y^{n_y} z^{n_z} \sum_i c_i \, exp(-a_i r^2).$$ (2)

We have recently used the time-dependent Schrödinger equation and a related time-dependent variational principle, to obtain complex time-dependent hydrogenic atomic orbitals (CTDHAO's) resulting from their interaction with a moving positive charge;[17] this procedure leads to optimized trial AOs with time-dependent orbital exponents. Here we use the Gaussian transform, which also appears in a generator coordinate context,[15] to express these CTDHAO's in terms of Gaussian functions. This allows us to construct time-dependent Gaussian basis sets at any given time.

The CTDHAO's have the form

$$\psi_{nlm}(\mathbf{r}, t) = R_{nl}[r; \zeta_{nl}(t)] Y_{lm}(\theta, \varphi),$$ (3)

where the time-dependence appears through the complex-valued parameters

$$\zeta_{nl}(t) = \lambda_{nl}(t) + i\kappa_{nl}(t).$$ (4)

We have found from the calculation of the time evolution of the complex parameters[17] that $\kappa \ll \lambda$ for charges moving at the thermal and hyperthermal velocities of interest in chemical applications; therefore we use the approximation

$$\zeta(t) \approx \lambda(t)$$ (5)

for the exponential parameters. From now on deal with HAO's whose varying effective charges have real values. We introduce a convenient change of integration variable in their Gaussian transform integral, before discretizing the variable by means of the Gauss-Legendre quadrature.[18] We can control the accuracy of our Gaussian fits by increasing the number of quadrature points in a systematic way. This allows us to obtain excellent fits to the HAOs without requiring least square fits or energy optimization.

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This paper is organized as follows. In sections 2 and 3 we show how to express the HAO's in terms of a Gaussian basis set of given size. In section 4 we give expressions for orthogonalizing the orbitals by the Gram-Schmidt procedure, and in section 5 we express them in terms of cartesian Gaussians.

2. HYDROGENIC ATOMIC ORBITALS

The radial parts of the 1s, 2s, and 2p HAO's are

$$R_{1s}(r; \lambda_{1s}) = 2\lambda_{1s}^{\frac{3}{2}} e^{-\lambda_{1s} r}, \tag{6}$$

$$R_{2s}(r; \lambda_{2s}) = \frac{1}{\sqrt{2}} \lambda_{2s}^{\frac{3}{2}} (1 - \frac{\lambda_{2s} r}{2}) e^{-\frac{\lambda_{2s} r}{2}}, \tag{7}$$

and

$$R_{2p}(r; \lambda_{2p}) = \frac{1}{2\sqrt{6}} \lambda_{2p}^{\frac{5}{2}} r e^{-\frac{\lambda_{2p} r}{2}}, \tag{8}$$

where the exponential parameters may change over time due to nuclear motions.

3. GAUSSIAN BASIS SETS

We next express the HAO's in terms of Gaussian transforms. This procedure allows us to choose the best set of Gaussian functions for example at any given time during the collision process.

A. The 1s orbital

In the 1s case, Eq. (6) becomes

$$R_{1s}(r; \zeta_{1s}) \approx 2\lambda_{1s}^{\frac{3}{2}} e^{-\lambda_{1s} r}. \tag{9}$$

In order to eliminate λ_{nl} in the pre-exponential term we make a rescaling[4]

$$\rho_{nl} = \lambda_{nl} r. \tag{10}$$

Now the normalized radial part of the orbital is

$$\overline{R}_{1s}(\rho_{1s}) = 2e^{-\rho_{1s}}, \tag{11}$$

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which satisfies

$$\langle \overline{R}_{1s}|\overline{R}_{1s}\rangle = \int_0^\infty d\rho_{1s}\ \overline{R}_{1s}(\rho_{1s})^2 = 1. \tag{12}$$

The Gaussian transform of $\overline{R}_{1s}(\rho_{1s})$ is[15]

$$\overline{R}_{1s}(\rho_{1s}) = 2e^{-\rho_{1s}} = \int_0^\infty \overline{f}_{1s}(\overline{\alpha})G(\overline{\alpha},\rho_{1s})d\overline{\alpha}, \tag{13}$$

where the weight function $\overline{f}_{1s}(\overline{\alpha})$ is

$$\overline{f}_{1s}(\overline{\alpha}) = (\pi\overline{\alpha}^3)^{-\frac{1}{2}}\ e^{-\frac{1}{4\overline{\alpha}}}, \tag{14}$$

and the generator function $G(\overline{\alpha},\rho_{1s})$ is

$$G(\overline{\alpha},\rho_{1s}) = e^{-\overline{\alpha}\rho_{1s}^2}, \tag{15}$$

with $\overline{\alpha}$ being the generator coordinate, i. e., the Gaussian exponential parameter.

We are interested in numerically evaluating Eq. (13) with a small number of Gaussian functions. So we make the following change of variables

$$\overline{\eta} = \exp(-\frac{1}{4\overline{\alpha}}). \tag{16}$$

which transforms the integration interval from $(0,\infty)$ to $(0,1)$.

Eq. (13) then becomes

$$\overline{R}_{1s}(\rho_{1s}) = \frac{2}{\sqrt{\pi}} \int_0^1 \frac{1}{(-\ln\eta)^{\frac{3}{2}}} \exp(\frac{\rho_{1s}^2}{4\ln\eta})d\eta. \tag{17}$$

Using the Gauss-Legendre quadrature[18] the integral in (17) becomes a summation and we have

$$\overline{R}_{1s}(\rho_{1s}) = \frac{2}{\sqrt{\pi}} \sum_{i=1}^N w_i \frac{1}{(-\ln\eta_i)^{\frac{3}{2}}} \exp(\frac{\rho_{1s}^2}{4\ln\eta_i}), \tag{18}$$

where the weights w_i and the abscissas η_i give the set of exponent factors and combination coefficients. We have used $N=6$ Gaussian functions throughout this paper.

Eq. (18) has two singular values at $\eta=0$ and $\eta=1$. In the present case, where we are using a small number of points, this is not a problem because the limit points are reasonably far from 0 and 1, respectively.

B. The 2s orbital

For the 2s orbital, Eq. (7), we have after the rescaling of Eq. (10) and normalization that

$$\overline{R}_{2s}(\rho_{2s}) = \frac{1}{\sqrt{2}}(1 - \frac{\rho_{2s}}{2})e^{-\frac{\rho_{2s}}{2}}, \tag{19}$$

which has the following Gaussian transform[15]

$$\overline{R}_{2s}(\rho_{2s}) = \int_0^\infty \overline{J}_{2s}(\overline{\alpha})G(\overline{\alpha}, \rho_{2s})d\overline{\alpha}, \tag{20}$$

where

$$\overline{J}_{2s}(\overline{\alpha}) = (8\pi\overline{\alpha}^3)^{-\frac{1}{2}}(2 - \frac{1}{2\overline{\alpha}})e^{-\frac{1}{4\overline{\alpha}}}, \tag{21}$$

and

$$G(\overline{\alpha}, \rho_{2s}) = e^{-\overline{\alpha}\frac{\rho_{2s}^2}{4}}. \tag{22}$$

Applying the change of variables of Eq. (16) to Eq. (20) we have

$$\overline{R}_{2s}(\rho_{2s}) = \frac{1}{\sqrt{2\pi}}\int_0^1 \frac{(2 + 2\ln\eta)}{(-\ln\eta)^{\frac{3}{2}}}\exp(\frac{\rho_{2s}^2}{16\ln\eta})d\eta, \tag{23}$$

which becomes, after application of the Gauss-Legendre quadrature

$$\overline{R}_{2s}(\rho_{2s}) = \frac{1}{\sqrt{2\pi}}\sum_{i=1}^N w_i\frac{(2 + 2\ln\eta_i)}{(-\ln\eta_i)^{\frac{3}{2}}}\exp(\frac{\rho_{2s}^2}{16\ln\eta_i}). \tag{24}$$

C. The 2p orbitals

For the 2p orbitals, Eq. (8), the equivalent of Eq. (19) is

$$\overline{R}_{2p}(\rho_{2p}) = \frac{1}{\sqrt{6}}\frac{\rho_{2p}}{2}e^{-\frac{\rho_{2p}}{2}}. \tag{25}$$

The Gaussian transform is[15]

$$\overline{R}_{2p}(\rho_{2p}) = \int_0^\infty \overline{J}_{2p}(\overline{\alpha})G(\overline{\alpha}, \rho_{2p})d\overline{\alpha}, \tag{26}$$

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where

$$\overline{f}_{2p}(\overline{\alpha}) = (24\pi\overline{\alpha}^5)^{-\frac{1}{2}} \left(\frac{1}{2\overline{\alpha}} - 1\right) e^{-\frac{1}{4\overline{\alpha}}}, \tag{27}$$

and

$$G(\overline{\alpha}, \rho_{2p}) = e^{-\overline{\alpha}\frac{\rho_{2p}^2}{4}}. \tag{28}$$

With the change of variables in Eq. (16), Eq. (26) becomes

$$\overline{R}_{2p}(\rho_{2p}) = \frac{1}{\sqrt{6\pi}} \int_0^1 \frac{(-1 - 2\ln\eta_i)}{(-\ln\eta_i)^{\frac{5}{2}}} \exp\left(\frac{\rho_{2p}^2}{16\ln\eta_i}\right) d\eta, \tag{29}$$

or

$$\overline{R}_{2p}(\rho_{2p}) = \frac{1}{\sqrt{6\pi}} \sum_{i=1}^N w_i \frac{(-1 - 2\ln\eta_i)}{(-\ln\eta_i)^{\frac{5}{2}}} \exp\left(\frac{\rho_{2p}^2}{16\ln\eta_i}\right). \tag{30}$$

With the use of Eq. (10) we can write Eqs. (18), (24), and (30) as

$$\overline{R}_{nl} = \sum_{i=1}^N c_{nl,i} \, e^{-a_{nl,i}r^2} \tag{31}$$

where the linear coefficients $c_{nl,i}$ and the exponents $a_{nl,i}$ (given in Table I) are expressed in terms of the weights and abscissas of Gauss-Legendre quadrature, which are given in Table II.

$R_{nl}(r; \lambda_{nl})$, Eqs. (6)-(8), can be obtained from $\overline{R}_{nl}(\rho_{nl})$ by noting that

$$\frac{R_{nl}(r; \lambda_{nl})}{\overline{R}_{nl}(\rho_{nl})} = \lambda_{nl}^{\frac{3}{2}}. \tag{32}$$

4. CARTESIAN GAUSSIAN REPRESENTATION

Because they have been preferred in molecular calculations, we are going to express our spherical Gaussian-type orbitals in terms of cartesian Gaussian functions.

We start out re-expressing the HAO's, Eq. (3), as

$$\psi_{nlm}(\mathbf{r}, t) = R_{nl}[r; \lambda_{nl}(t)] r^{-l} r^l Y_{lm}(\theta, \varphi), \tag{33}$$

where the solid spherical harmonics, $r^l Y_{lm}(\theta, \varphi)$, correspond to linear combinations of the integer powers of the cartesian coordinates.

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In the case of s orbitals, $l=0$ and the cartesian and spherical representations are the same. In the case of 2p orbitals we have

$$\psi_{2p_k}(\mathbf{r},t) = k\frac{1}{4\sqrt{2\pi}}\lambda_{2p}^{\frac{1}{2}}\, e^{-\frac{\lambda_{2p}}{2}\, r}, \tag{34}$$

where k stands for x, y, and z.

Applying the rescaling of Eq. (10) to the "radial" part, Eq. (34) becomes

$$\psi_{2p_k}(\mathbf{r},t) = k\frac{1}{4\sqrt{2\pi}}\lambda_{2p}^{\frac{1}{2}}\, e^{-\frac{\rho_{2p}}{2}}, \tag{35}$$

which has the following Gaussian transform

$$\psi_{2p_k}(\mathbf{r},t) = k\frac{1}{4\sqrt{2\pi}}\lambda_{2p}^{\frac{1}{2}}\frac{1}{2\sqrt{\pi}}\int_0^\infty \overline{\alpha}^{-\frac{3}{2}}\, \exp(-\frac{1}{4\overline{\alpha}})\exp(-\overline{\alpha}\frac{\rho_{2p}^2}{4})\, d\alpha. \tag{36}$$

Applying the change of variables (16) and the Gauss-Legendre quadrature [18] to Eq. (36) we have

$$\psi_{2p_k}(\mathbf{r},t) = k\frac{1}{4\pi\sqrt{2}}\lambda_{2p}^{\frac{1}{2}}\sum_{i=1}^N \frac{w_i}{(-\ln\eta_i)^{\frac{3}{2}}}\exp(\frac{\rho_{2p}^2}{16\ln\eta_i})\,. \tag{37}$$

If we express Eq. (37) like we did in Eq. (31) we have that

$$\psi_{2p_k}(\mathbf{r},t) = k\sum_{i=1}^N c_{2p,i}^{(cart)}\exp(-a_{2p,i}r^2)\,. \tag{38}$$

where $c_{2p,i}^{(cart)}$ and $a_{2p,i}$ are given in table I.

5. GRAM-SCHMIDT ORTHOGONALIZATION

The exact hydrogen-like orbitals are orthonormal, i. e.,

$$\langle\psi_{nlm}\mid\psi_{n'l'm'}\rangle = \delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{39}$$

However when we calculate Eq. (39) using six Gaussian functions we obtained 0.015976, 1.0015, 0.892141, and 0.942533 for the 1s-2s, 1s-1s, 2s-2s, and 2p-2p overlaps, respectively. Therefore we decided to orthogonalize the orbitals with the Gram-Schmidt procedure.[19]

We begin with the normalization of $\overline{R}_{1s}$. If we take

$$\overline{R}_{1s}^{(N)}(\rho_{1s}) = N_{1s}\overline{R}_{1s}(\rho_{1s}),$$ (40)

and impose that

$$\langle \overline{R}_{1s}^{(N)} | \overline{R}_{1s}^{(N)} \rangle = \int_0^\infty d\rho_{1s}\, \overline{R}_{1s}^N(\rho_{1s})^2 = 1,$$ (41)

then we have that

$$N_{1s} = \frac{1}{\sqrt{\langle \overline{R}_{1s} | \overline{R}_{1s} \rangle}},$$ (42)

where

$$\langle \overline{R}_{1s} | \overline{R}_{1s} \rangle = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{w_i}{\sqrt{-\ln \eta_i}} \frac{w_j}{\sqrt{-\ln \eta_j}}$$
$$\times \left[\frac{1}{4(-\ln \eta_i)} + \frac{1}{4(-\ln \eta_j)}\right]^{-\frac{3}{2}}.$$ (43)

Next we want to orthogonalize the 2s orbital. To do this we take the new orthogonal unnormalized 2s orbital, $\overline{R}_{2s}'(\rho_{2s})$, as

$$\overline{R}_{2s}'(\rho_{2s}) = \overline{R}_{2s}(\rho_{2s}) + \beta \overline{R}_{1s}^{(N)}(\rho_{1s}).$$ (44)

The requirement that $\overline{R}_{2s}'(\rho_{2s})$ be orthogonal to $\overline{R}_{1s}^{(N)}(\rho_{1s})$ allows us to determine β,

$$\beta = -\langle \overline{R}_{2s} | \overline{R}_{1s}^{(N)} \rangle =$$
$$= N_{1s} \frac{1}{2\sqrt{2\pi}} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{w_i}{\sqrt{-\ln \eta_i}} \frac{w_j(2 + 2\ln \eta_j)}{\sqrt{-\ln \eta_j}} \left[\frac{1}{4(-\ln \eta_i)} + \frac{1}{16(-\ln \eta_j)}\right]^{-\frac{3}{2}}.$$ (45)

In the present case $\beta = -0.015963$.

Now we normalize the 2s orbital by expressing it as

$$\overline{R}_{2s}'^{(N)}(\rho_{2s}) = N_{2s}'\overline{R}_{2s}'(\rho_{2s}).$$ (46)

Normalizing $\overline{R}_{2s}'^{(N)}$ to unity gives us

$$N_{2s}' = \frac{1}{\sqrt{\langle \overline{R}_{2s}' | \overline{R}_{2s}' \rangle}},$$ (47)

where

$$\langle \overline{R}'_{2s} | \overline{R}'_{2s} \rangle = \langle \overline{R}_{2s}(\rho_{2s}) | \overline{R}_{2s}(\rho_{2s}) \rangle - \beta^2 =$$

$$= \frac{1}{8\sqrt{\pi}} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{w_i(2 + 2\ln \eta_i)}{\sqrt{-\ln \eta_i}} \frac{w_j(2 + 2\ln \eta_j)}{\sqrt{-\ln \eta_j}} [\frac{1}{16(-\ln \eta_i)} + \frac{1}{16(-\ln \eta_j)}]^{-\frac{3}{2}} - \beta^2. \qquad (48)$$

Since we cannot represent $\overline{R}'_{2s}(\rho_{2s})$, Eq. (44), as a single summation, we have instead shown, in Table III, the normalized $\overline{R}_{2s}(\rho_{2s})$

$$\overline{R}_{2s}^{(N)}(\rho_{2s}) = N_{2s} \overline{R}_{2s}(\rho_{2s}), \qquad (49)$$

where

$$N_{2s} = \frac{1}{\sqrt{\langle \overline{R}_{2s} | \overline{R}_{2s} \rangle}}. \qquad (50)$$

In the case of 2p orbitals we just normalize them to unity because their spherical harmonics make them orthogonal to s-orbitals. So the normalized radial part is

$$\overline{R}_{2p}^{(N)}(\rho_{2p}) = N_{2p} \overline{R}_{2p}(\rho_{2p}), \qquad (51)$$

where (by the normalization condition)

$$N_{2p} = \frac{1}{\sqrt{\langle \overline{R}_{2p} | \overline{R}_{2p} \rangle}}, \qquad (52)$$

with

$$\langle \overline{R}_{2p} | \overline{R}_{2p} \rangle =$$

$$= \frac{1}{24\sqrt{\pi}} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{w_i(-1 - 2\ln \eta_i)}{\sqrt{-\ln \eta_i}} \frac{w_j(-1 - 2\ln \eta_j)}{\sqrt{-\ln \eta_j}} [\frac{1}{16(-\ln \eta_i)} + \frac{1}{16(-\ln \eta_j)}]^{-\frac{5}{2}}. \qquad (53)$$

In the case or cartesian 2p orbitals we normalize the whole orbital to unity , i. e.,

$$\psi_{2p_k}^{(N)}(\mathbf{r}, t) = N_{2p_k} \psi_{2p_k}(\mathbf{r}, t) = N_{2p_k} k \frac{\lambda_{2p}^{\frac{5}{2}}}{4\pi\sqrt{2}} \sum_{i=1}^{N} \frac{w_i}{(-\ln \eta_i)^{\frac{5}{2}}} \exp(\frac{\rho_{2p}^2}{16 \ln \eta_i}), \qquad (54)$$

where (by the normalization condition)

$$N_{2p_k} = \frac{1}{\sqrt{\langle \psi_{2p_k} | \psi_{2p_k} \rangle}}, \qquad (55)$$

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integrals in molecular calculations. An alternative is to orthonormalize the orbitals. The Gram-Schmidt procedure was found to be convenient for this purpose; it can be implemented with the expressions we presented in Section 5, and require only a knowledge of the Gauss-Legendre quadrature points. The small calculated value of the β coefficient there suggests that forcing more strict orthogonality will have only a small effect on molecular densities.

The figures show that the behavior of the physical HAO's can be well represented over wide distances, as required for molecular interaction studies. The largest discrepancy is found near the origen for the cusp behaviour, as expected. This region of the atomic distances is however inaccessible for thermal and hyperthermal collision velocities so that an error in that region would not have a noticeable effect on collisional properties such as cross sections. The long range behaviour of the HAOs is very well reproduced and indicates that the constructed orbitals would have the correct interatomic overlaps required for the description of electronic rearrangement in molecular interactions.

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Table I

Linear coefficients c_i and exponents a_i for the Gaussian expansion of the HAO's.

Orbital	c_i	a_i
1s	$\frac{2}{\sqrt{\pi}}\frac{w_i}{(-\ln\eta_i)^{\frac{3}{2}}}$	$-\frac{\lambda_{1s}^2}{4\ln\eta_i}$
2s	$\frac{1}{\sqrt{2\pi}}w_i\frac{(2+2\ln\eta_i)}{(-\ln\eta_i)^{\frac{5}{2}}}$	$-\frac{\lambda_{2s}^2}{16\ln\eta_i}$
2p	$\frac{1}{\sqrt{6\pi}}w_i\frac{(-1-2\ln\eta_i)}{(-\ln\eta_i)^{\frac{5}{2}}}$	$-\frac{\lambda_{2p}^2}{16\ln\eta_i}$
$2p^{(cart)}$	$\frac{1}{4\pi\sqrt{2}}w_i\frac{\lambda_{2p}^{\frac{5}{2}}}{(-\ln\eta_i)^{\frac{5}{2}}}$	$-\frac{\lambda_{2p}^2}{16\ln\eta_i}$

Table II

Weights w_i and abscissas η_i for the Gauss-Legendre quadrature with $N=6$.

w_i	η_i
0.085662	0.033765
0.180381	0.169395
0.233957	0.380690
0.233957	0.619310
0.180381	0.830605
0.085662	0.966235

Table III

Numerical values of linear coefficients c_i and exponents a_i for normalized orbitals with $\lambda_{nl}=1.0$..

i	$c_{1s,i}$	$a_{1s,i}$	$c_{2s,i}$	$a_{2s,i} =$ $a_{2p,i}$	$c_{2p,i}$	$c_{2p,i}^{(cart)}$
1	0.052469	0.073783	-0.093888	0.018446	0.063778	0.002621
2	0.152629	0.140804	-0.406076	0.035201	0.081931	0.007626
3	0.268416	0.258861	0.006884	0.064715	0.052614	0.013412
4	0.381074	0.521758	0.148709	0.130439	-0.003344	0.019041
5	0.472074	1.346976	0.288046	0.336744	-0.062462	0.023588
6	0.521129	7.278401	0.377034	1.819600	-0.102124	0.026039

Figure Captions

Figure 1 — Comparison between the exact radial part of the 1s normalized hydrogenic orbital and the corresponding numerical one obtained in this work with 6 Gaussians.

Figure 2 — The same as figure 1 for the 2s orbital.

Figure 3 — The same as figure 1 for the 2p orbital.

Figure 4 — Comparison between the exact "radial" part of the cartesian 2p orbital, given by $(3/4\pi)^{-1/2} r^{-1} R_{2p}$ and the corresponding numerical values obtained in this work with 6 Gaussians.
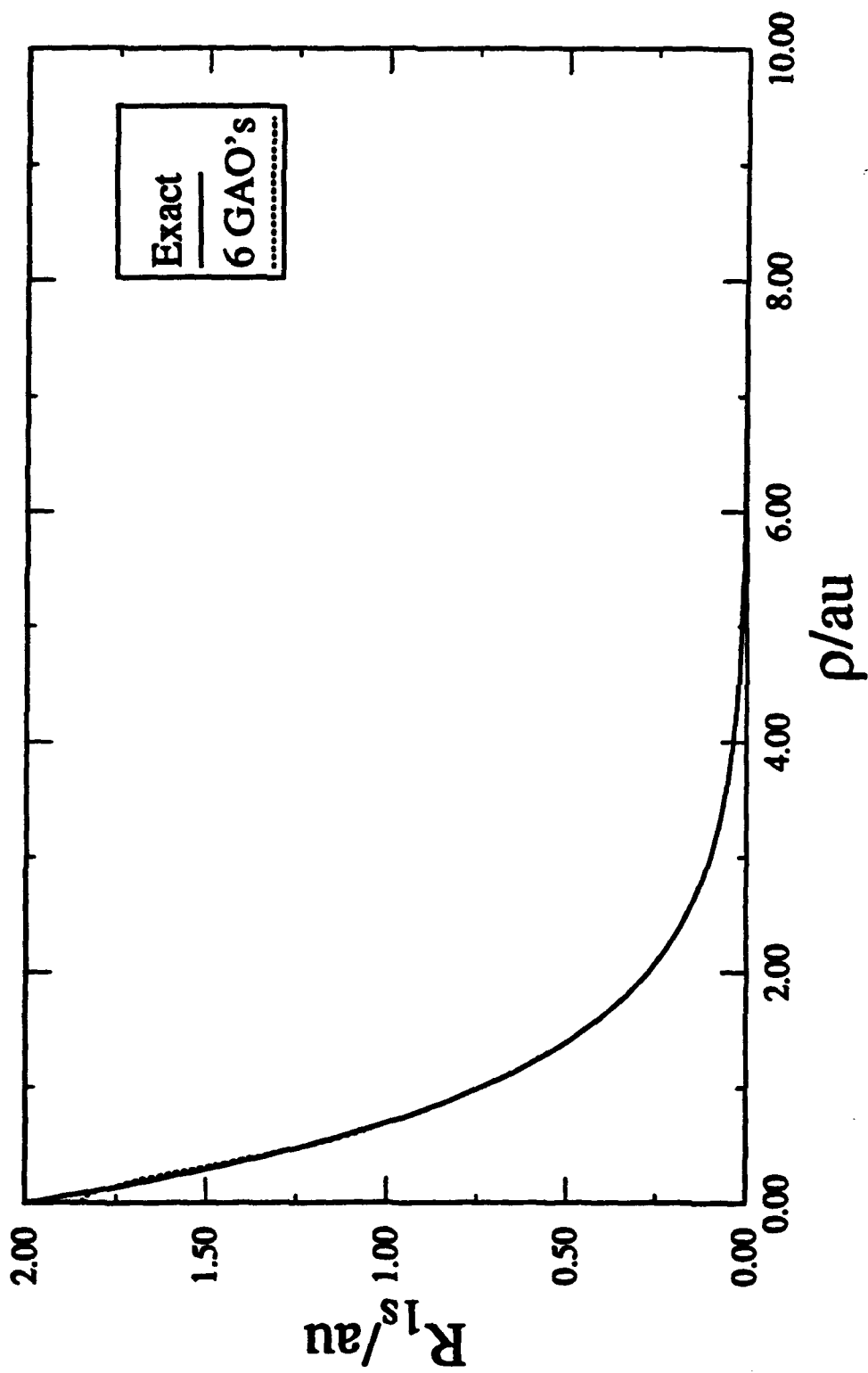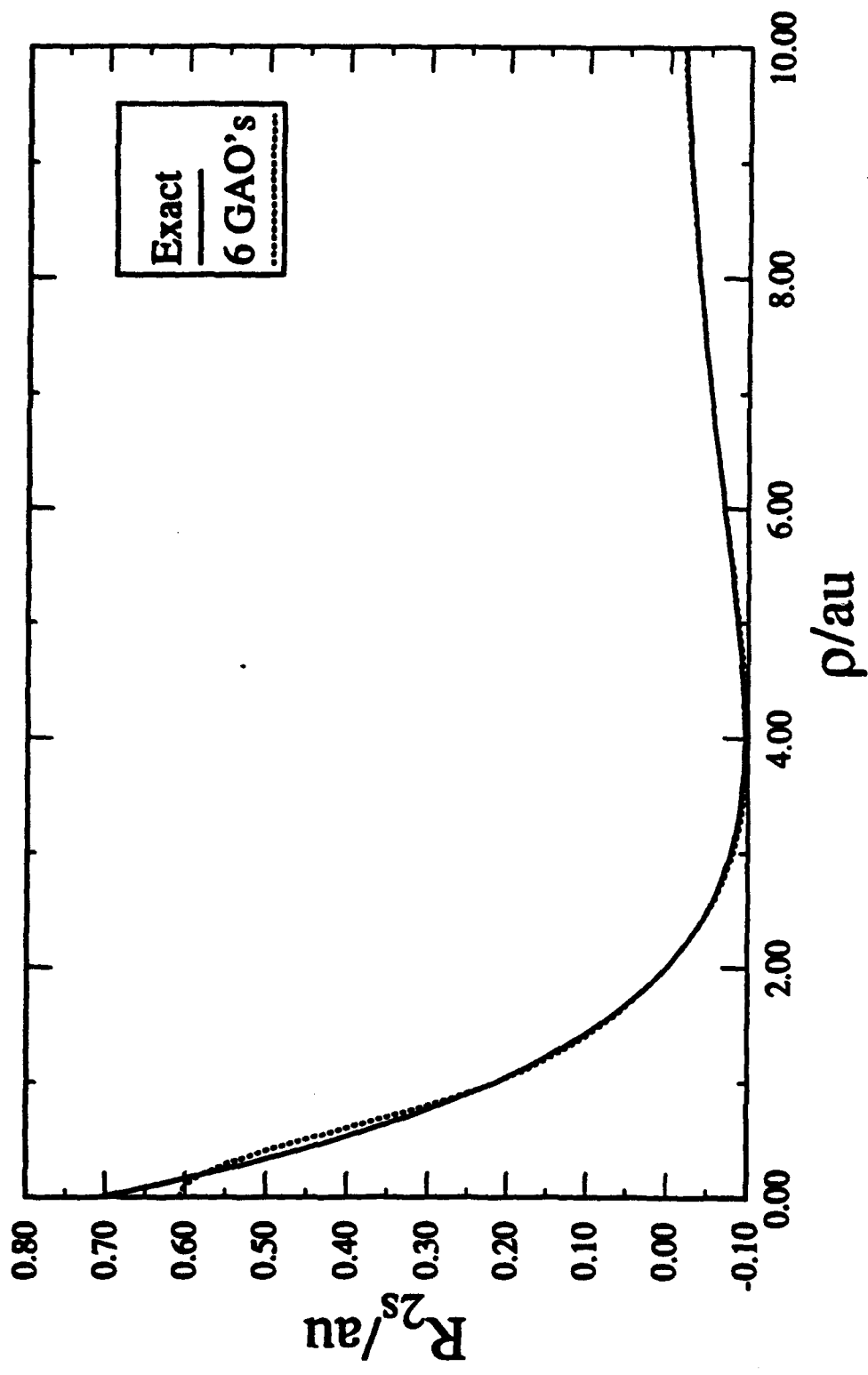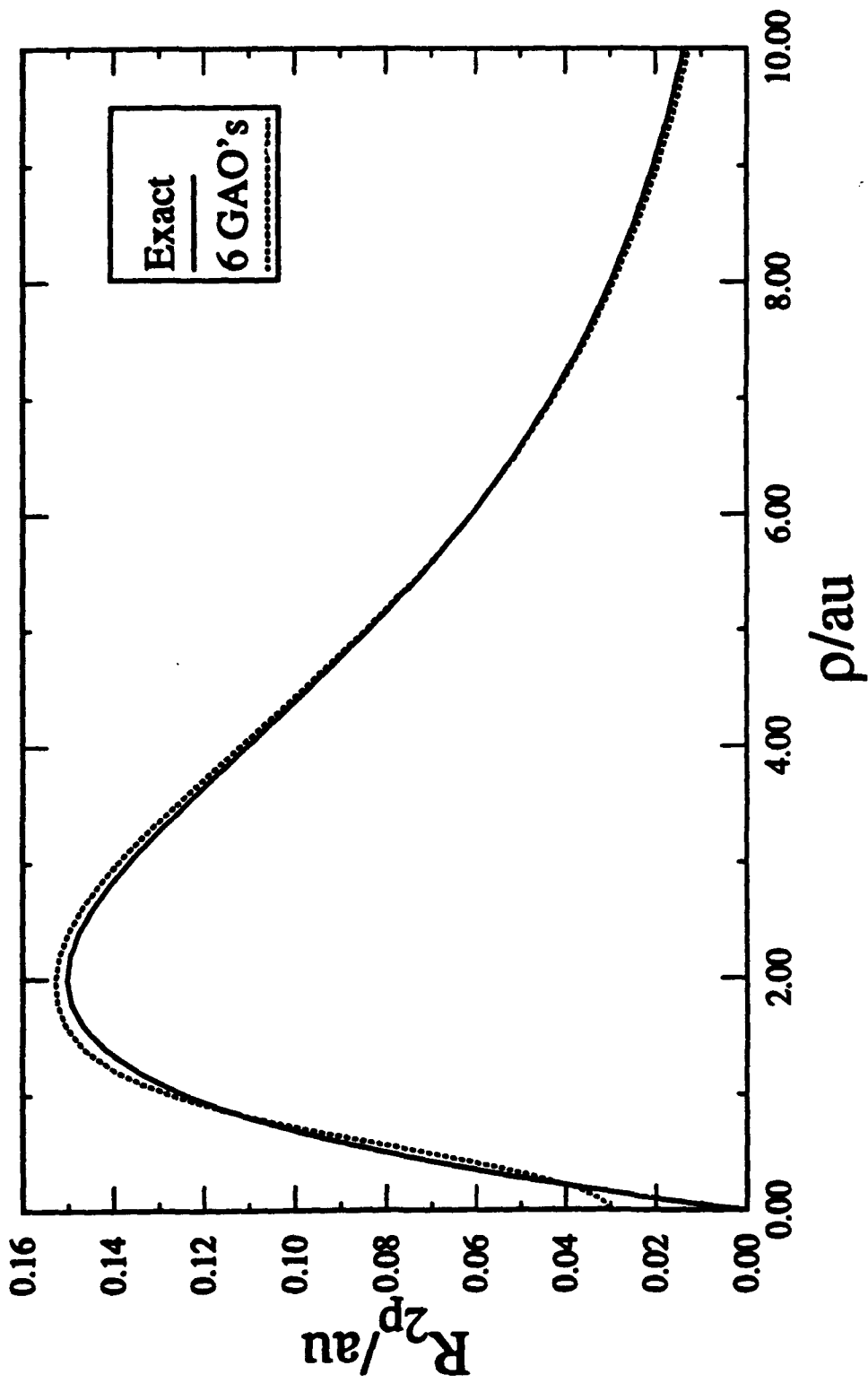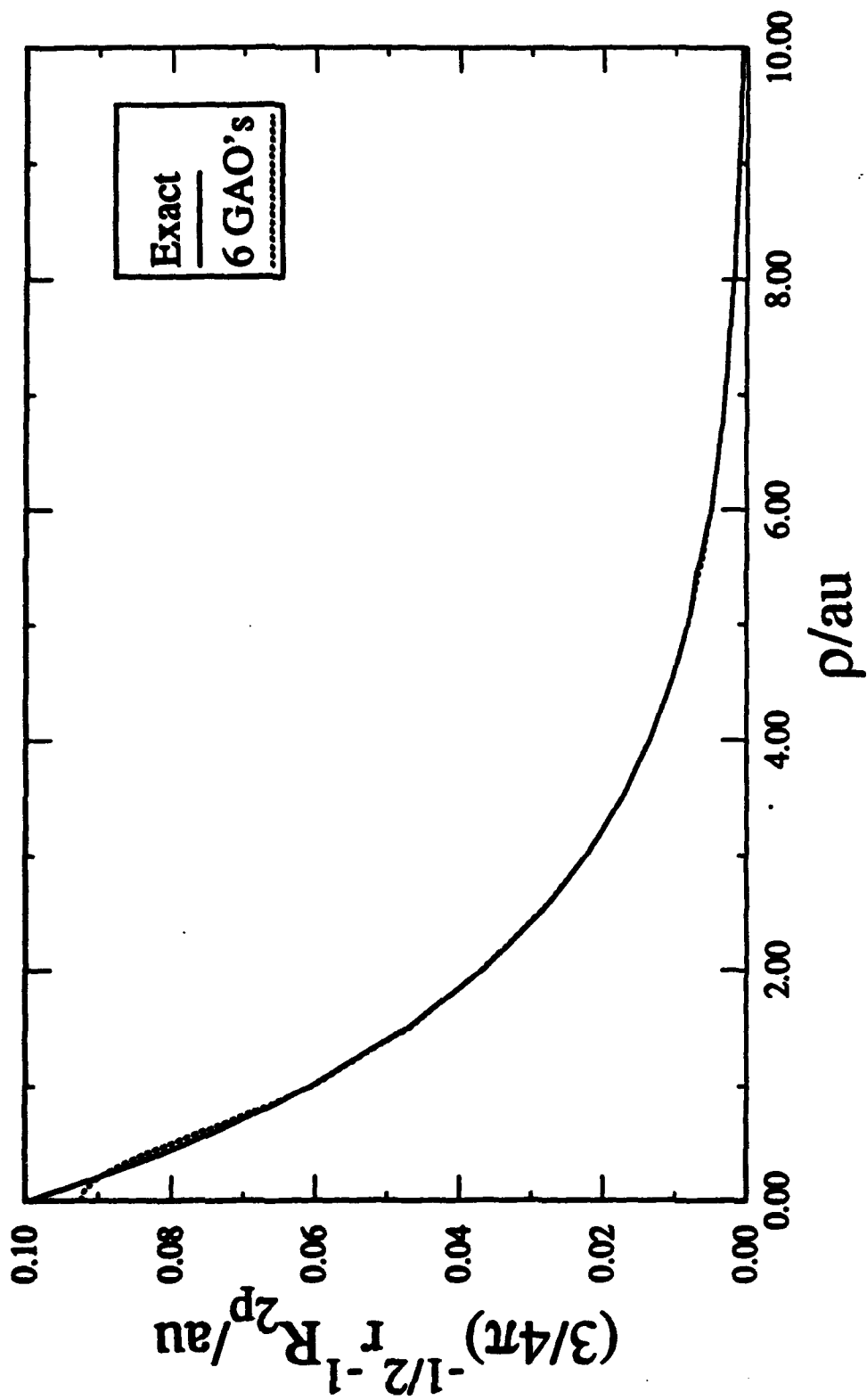
Figure 1

Figure 2

Figure 3

Figure 4