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Polyatomic SCF Calculations with Numerical Orbitals.

II. Methods to Reduce Integration and Truncation Error

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We discuss an improved technique for handling the Coulomb singularity in the momentum space Hartree–Fock equations. This method improves the quality of numerical orbitals by significantly reducing the integration error. We also examine a number of ways of reducing truncation error in these calculations.

1. INTRODUCTION

When solving the molecular Hartree–Fock equations, one has a choice of describing molecular orbitals either as an expansion in some simple basis set or as an organized set of computed values, i.e., numerically. Although both methods must ultimately yield the same results, each has certain advantages and disadvantages depending on the computational circumstances. Calculations which use basis sets of atomic-based functions (i.e., LCAO calculations) provide a quick, easy estimate of molecular orbitals and a great deal of work has gone into computing the necessary sets of primitive functions that this method requires. This approach, however, often needs a large number of basis functions to achieve highly accurate results. Usually this number can be substantially reduced by optimizing the primitives on the molecule of interest rather than on the isolated atoms. Such calculations are quite expensive, however, and so are rarely done [1].

In contrast to the large number of calculations today which use basis sets, numerical orbital calculations are still quite rare. This is due in part to their relatively recent implementation. Numerical orbital calculations were first performed on atoms [2] and later on diatomics [3] because the Coulomb singularities in these systems could be eliminated analytically. Those calculations which have been done produced exceptionally accurate results. Because these methods are explicitly designed to compute a specific subclass of molecules, they cannot be used to study polyatomic systems. In the first paper of this series [4] we examined a simple algorithm for generating numerical orbitals for general polyatomics. To avoid the

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numerous singularities which exist in position space, we use the momentum space representation of the Hartree–Fock equations [5, 6]. Here only one singularity exists at the origin and we were able to numerically remove this singularity by adding and subtracting it away. This algorithm produced results of four to five significant figure accuracy on a number of two-electron systems. These calculations also showed that numerical integration error and truncation error (caused by integrating over a finite region) were the major impediments to increased accuracy. In this paper we compare a new procedure for treating the Coulomb singularity with our previous method and we examine a number of ways of decreasing the truncation error.

2. THE HARTREE–FOCK EQUATION IN MOMENTUM SPACE

In position space the (restricted) Hartree–Fock equations for closed shell molecules have the form

$$\begin{aligned}\varepsilon_i \phi_i(\mathbf{r}) &= -\frac{\nabla^2}{2}\phi_i(\mathbf{r}) - \sum_{a=1}^{\#\text{Atoms}} \frac{Z_a}{|\mathbf{r}-\mathbf{R}_a|}\phi_i(\mathbf{r}) \\ &\quad + 2\sum_j \int d^3r' \frac{\phi_j^*(\mathbf{r}')\,\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}) \\ &\quad - \sum_j \int d^3r' \frac{\phi_j^*(\mathbf{r}')\,\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r}) \\ &= -\frac{\nabla^2}{2}\phi_i(\mathbf{r}) - W(\mathbf{r})\,\phi_i(\mathbf{r}) \\ &\quad + 2\sum_j W_{jj}(\mathbf{r})\,\phi_i(\mathbf{r}) - \sum_j W_{ji}(\mathbf{r})\,\phi_j(\mathbf{r}), \end{aligned} \tag{1}$$

where ε_i is the ith orbital energy, $\mathbf{R}_a$ is the ath nuclear position,

$$W(\mathbf{r}) = \sum_{a=1}^{\#\text{Atoms}} Z_a v_a(\mathbf{r}) \tag{2}$$

$$W_{ij}(\mathbf{r}) = S_{ij} \otimes v(\mathbf{r}) \tag{3}$$

and where

$$v_a(\mathbf{r}) = 1/|\mathbf{r}-\mathbf{R}_a| \tag{4}$$

$$v(\mathbf{r}) = 1/\mathbf{r} \tag{5}$$

$$S_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r})\,\phi_j(\mathbf{r}). \tag{6}$$

Above we give both the standard integral form and one which uses the convolution relationship

$$f \otimes g(\mathbf{r}) = \int d^3r' f(\mathbf{r}')\, g(\mathbf{r} - \mathbf{r}') \tag{7}$$

to describe the electron–electron part of the Coulomb potential. This latter version is especially useful when converting to momentum space. Using Fourier transforms and the relationship

$$\int d^3q f(\mathbf{q})\, g(\mathbf{p} - \mathbf{q}) = f \otimes g(\mathbf{p}) = (2\pi)^{3/2}\, [f(\mathbf{r})\, g(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}), \tag{8}$$

where

$$f(\mathbf{r}) = [f(\mathbf{p})]^{\mathrm{T}}\, (\mathbf{r}) \tag{9}$$

and

$$g(\mathbf{r}) = [g(\mathbf{p})]^{\mathrm{T}}\, (\mathbf{r}) \tag{10}$$

the Hartree–Fock equations become

$$\begin{aligned} \varepsilon_i \phi_i(\mathbf{p}) &= \frac{p^2}{2}\, \phi_i(\mathbf{p}) - \int d^3q W(\mathbf{q})\, \phi_i(\mathbf{p} - \mathbf{q}) \\ &\quad + 2 \sum_j \int d^3q W_{jj}(\mathbf{q})\, \phi_i(\mathbf{p} - \mathbf{q}) - \sum_j \int d^3q W_{ji}(\mathbf{q})\, \phi_j(\mathbf{p} - \mathbf{q}) \\ &= \frac{p^2}{2}\, \phi_i(\mathbf{p}) - W \otimes \phi_i(\mathbf{p}) + \sum_j W_{jj} \otimes \phi_i(\mathbf{p}) - \sum_j W_{ji} \otimes \phi_j(\mathbf{p}), \end{aligned} \tag{11}$$

where

$$W(\mathbf{p}) = (2\pi)^{-3/2}\, S(\mathbf{p})\, v(\mathbf{p}) \tag{12}$$

$$W_{ij}(\mathbf{p}) = (2\pi)^{-3/2}\, S_{ij}(\mathbf{p})\, v(\mathbf{p}) \tag{13}$$

and where

$$v(\mathbf{p}) = [v(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}) = (2/\pi)^{1/2}/p^2 \tag{14}$$

$$S(\mathbf{p}) = \sum_{a=1}^{\#\,\mathrm{Atoms}} Z_a e^{i\mathbf{p}\ \mathbf{R}_a} \tag{15}$$

$$S_{ij}(\mathbf{p}) = \int d^3q \phi_i^*(\mathbf{q})\, \phi_j(\mathbf{p} + \mathbf{q}) = (2\pi)^{3/2}\, [S_{ij}(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}) = \phi_i^* \otimes \phi_j(\mathbf{p}). \tag{16}$$

Although we have written Eq. (1) and (11) as being mathematically equivalent to one another, their numerical solutions have quite different requirements and only in the limit of an infinite grid would we expect to obtain the same result. For polyatomic systems it is easier to numerically solve the Hartree–Fock equations in momentum space because only a single, removable singularity exists. In Ref. [4] we proposed the following algorithm to solve such systems:

Step 1. Initialize the orbitals. One possible choice is the 1*s* orbital in momentum space

$$\phi_i(\mathbf{p}) = \mathrm{Norm}/(p^2 - 2\varepsilon_i)^2. \qquad (17)$$

Step 2. Normalize the orbitals

$$1 = \mathrm{Norm}^2 \int d^3p\, |\phi_i(\mathbf{p})|^2. \qquad (18)$$

Step 3. Gram–Schmidt orthogonalize each orbital

$$\phi^{\mathrm{orth}}_{i+1}(\mathbf{p}) = \sum_{j=1}^{i} \left\{ \phi_{i+1}(\mathbf{p}) - \phi_j^{\mathrm{orth}}(\mathbf{p}) \int d^3q\, \phi_{i+1}(\mathbf{q})\, \phi_j^{\mathrm{orth}}(\mathbf{q}) \right\}. \qquad (19)$$

Hereafter, all orbitals are assumed to be orthogonal.

Step 4. Compute the convolutions

$$S_{ij}(\mathbf{p}) = (2\pi)^{3/2}\, [\hat{\phi}_i^*(\mathbf{r})\, \hat{\phi}_j(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}), \qquad (20)$$

where

$$\hat{\phi}_i(\mathbf{r}) = [\phi_i(\mathbf{p})]^{\mathrm{T}}\, (\mathbf{r}). \qquad (21)$$

Step 5. Compute the SCF energy

$$E = \sum_i \int d^3p\, \phi_i^*(\mathbf{p})\, p^2 \phi_i(\mathbf{p}) - 2 \sum_i \int d^3p\, W(\mathbf{p})\, S_{ii}^*(\mathbf{p})$$
$$+ 2 \sum_{i,j} \int d^3p\, W_{ii}(\mathbf{p})\, S_{jj}^*(\mathbf{p}) - \sum_{i,j} \int d^3p\, W_{ij}(\mathbf{p})\, S_{ij}^*(\mathbf{p}). \qquad (22)$$

Step 6. Compute the convolutions

$$C_i(\mathbf{p}) = [\hat{W}(\mathbf{r})\, \hat{\phi}_i(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}) - 2 \sum_j [\hat{W}_{jj}(\mathbf{r})\, \hat{\phi}_i(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p})$$
$$+ \sum_j [\hat{W}_{ji}(\mathbf{r})\, \hat{\phi}_j(\mathbf{r})]^{\mathrm{T}}\, (\mathbf{p}), \qquad (23)$$

where

$$\hat{W}_{ij}(\mathbf{r}) = [W_{ij}(\mathbf{p})]^{\mathrm{T}}(\mathbf{r}) \tag{24}$$

and

$$\hat{W}(\mathbf{r}) = [W(\mathbf{p})]^{\mathrm{T}}(\mathbf{r}). \tag{25}$$

Step 7. Diagonalize the Fock matrix

$$\sum_j \{F_{ij} - \varepsilon_i^{\mathrm{new}}\,\delta_{ij}\}\,c_{ij}^{\mathrm{new}} = 0, \tag{26}$$

where

$$F_{ij} = \int d^3p \left\{\phi_i^*(\mathbf{p})\frac{p}{2}\phi_j(\mathbf{p}) + \phi_i^*(\mathbf{p})\,C_j(\mathbf{p})\right\} \tag{27}$$

to get the orbital energies and the eigenvector coefficients.

Step 8. Compute the improved approximation to the orbitals

$$\phi_i^{\mathrm{new}}(\mathbf{p}) = \sum_j \phi_j(\mathbf{p})\,c_{ij}^{\mathrm{new}}. \tag{28}$$

If only one orbital exists then

$$\phi_1^{\mathrm{new}}(\mathbf{p}) = C_1(\mathbf{p})/(p^2/2 - \varepsilon_1^{\mathrm{new}}). \tag{29}$$

Step 9. Normalize the new guess

$$1 = \mathrm{Norm}^2 \int d^3p\,|\phi_i^{\mathrm{new}}(\mathbf{p})|^2. \tag{30}$$

Step 10. Test for convergence

$$\sigma_i^2 = \int d^3p\,|\phi_i^{\mathrm{new}}(\mathbf{p}) - \phi_i(\mathbf{p})|^2. \tag{31}$$

Step 11. Return to Step 3 unless converged (using whatever criterion—energy, σ, or ε).

Because the time-limiting step in the solution of Eq. (11) is the evaluation of the convolutions, we calculate each convolution using a cascade of fast Fourier transforms (FFTs). This method scales as $N \operatorname{Log}_2 N$, where N is the total number of grid points used, in contrast to all forms of direct evaluation which scale as N^2. In addition, each step of our algorithm is easily changed to vector form, so the full power of modern supercomputers can be applied to it. This is not true of direct evaluation methods since they require grid interpolations to evaluate the convolutions. For these reasons we believe that Eq. (17)–(31) represent the best algorithm for computing numerical orbitals.

3. HANDLING THE COULOMB SINGULARITY

FFTs require a Cartesian grid with equidistant points. On such a grid, Eq. (17)–(31) contain two types of singular integrals. These can be generalized as

$$\int d^3p A(\mathbf{p})\, v(\mathbf{p}) \tag{32}$$

and

$$\int d^3p A(\mathbf{p})\, v(\mathbf{p})\, e^{-i\mathbf{p}\cdot\mathbf{r}}, \tag{33}$$

where $A(\mathbf{p})$ is the nonsingular part of the integrand and $v(\mathbf{p})$ is defined in Eq. (14) as $1/p^2$. Below we examine three ways of accurately integrating these functions. Method 1 numerically removes the singularity by adding and subtracting the point $p=0$. Method 2 also adds and subtracts the point $p=0$ but includes second derivatives of the integrand to more accurately model the behavior of $A(\mathbf{p})$ at the origin. Method 3 numerically eliminates this singularity by replacing $v(\mathbf{p})$ with the transform of $v(\mathbf{r})$ over a finite cube.

Method 1. By adding and subtracting the point $p=0$ in Eq. (32), this integral can be rewritten as

$$\int d^3p\{A(\mathbf{p})-A(0)\}/p^2+A(0)\int d^3p/p^2. \tag{34}$$

If the origin for the nuclear position vectors $\mathbf{R}_a$ is placed at the center of charge and no exchange terms are present, the leading term of $\{A(\mathbf{p})-A(0)\}$ is proportional to p^2 [7] and so the first part of Eq. (34) is smooth everywhere. Since our integration points are equidistantly spaced over a cubical region, one simple method of evaluating this integral is by trapezoidal integration

$$\int d^3p\{A(\mathbf{p})-A(0)\}/p^2 \sim h^3 \sum_{klm} F_{klm}, \tag{35}$$

where

$$\begin{aligned} F_{klm} &= [A(p_{klm})-A(0)]/p_{klm}^2 \qquad (\text{for } p_{klm}\neq 0)\\ F(0) &= 0 \end{aligned} \tag{36}$$

and where h is the spacing between points. Over the cube $[-P, P]$ the second part of Eq. (34) has the value $A(0)$ 15.34824844 P. Similarly, Eq. (33) can be rewritten as

$$\int d^3p\{A(\mathbf{p})-A(0)\}\, e^{-i\mathbf{p}\cdot\mathbf{r}}/p^2 + A(0)\int d^3p e^{-i\mathbf{p}\cdot\mathbf{r}}/p^2. \tag{37}$$

The first part of this expression is again smooth everywhere and can be evaluated using an FFT

$$\int d^3p\{A(\mathbf{p})-A(0)\}\, e^{-i\mathbf{p}\cdot\mathbf{r}}/p^2 \sim h^3[F_{klm}]^{\mathrm{T}}\,(\mathbf{r}). \tag{38}$$

Because the second part of Eq. (37) is a function of $\mathbf{r}$, its evaluation is somewhat more complicated. One very stable method of computing this function is to transform it into the form

$$\int_{\text{cube}} d^3pe^{-i\mathbf{p}\cdot\mathbf{r}}/p^2 = \int_0^{\infty} ds\, I_x\, I_y\, I_z, \tag{39}$$

where

$$I_x = \int_{-P}^{P} dxe^{-(sx^2+ir_xx)},\quad I_y = \int_{-P}^{P} dye^{-(sy^2+ir_yy)},\quad I_z = \int_{-P}^{P} dze^{-(sz^2+ir_zz)}.$$

In this representation the inner integrations can be solved analytically

$$I_x = e^{-r_x^2/4s}\,(\pi/s)^{1/2}\,\mathrm{Re}(1-e^{-z^2}w(iz)), \tag{40}$$

where

$$z = (Ps^{1/2}) + i(r_x/(2s^{1/2}))$$

and where $w(iz)$ is of a form of the complex error function which can be evaluated very accurately [8]. We compute the outer integration over s in Eq. (39) in two parts. In the interval $[0, S]$, where S is some maximum value of s (e.g., $S = 20P$), a small Gaussian quadrature (10–20 points) is used. For values larger than S the integral is evaluated analytically by approximating $w(iz)$ with unity.

When exchange terms are present, the leading term of $\{A(\mathbf{p})-A(0)\}$ is proportional to $\mathbf{p}$. On a finite grid this behavior leads to a singularity at the origin and therefore this method fails.

Method 2. Rather than simply setting $F(0)=0$ as we do in Eq. (36), the first contribution from the series expansion of $\{A(\mathbf{p}-A(0)\}$

$$F(0) = [A_{xx}(0)+A_{yy}(0)+A_{zz}(0)]/6 \tag{41}$$

can be used. This change should more accurately model the behavior of this function around $p=0$ and improve the numerical integration. Here A_{ii} $(i = x, y, z)$

are the second derivatives of $A(\mathbf{p})$ and are formed numerically using a 5-point difference formula. Additional contributions would contain factors of order h^5 or higher and so are not included. Like Method 1, this method of treating the singularity is expected to be applicable only when no exchange terms are present.

Method 3. In Eq. (32) and (33) the singularity, $1/p^2$, exists because the transformation of $v(\mathbf{r})$ in Eq. (14) has been performed exactly over all space. Calculations by Coldwell [9] suggest, however, that this transformation should be treated like all our other transformations, i.e, over a finite cube. Because $v(\mathbf{p})$ is no longer computed over all space, no singularity exists. The result is that Eq. (32) and (33) now have the form

$$\int d^3p A(\mathbf{p})\, \hat{v}(\mathbf{p}) \tag{42}$$

and

$$\int d^3p A(\mathbf{p})\, \hat{v}(\mathbf{p})\, e^{-i\mathbf{p}\cdot\mathbf{r}} \tag{43}$$

and can now be numerically integrated directly. The function $\hat{v}(\mathbf{p})$ is best evaluated using a transform similar to the one in Eq. (39)

$$\hat{v}(\mathbf{p}) = (2\pi)^{-3/2} \int_{\text{cube}} d^3r e^{i\mathbf{p}\cdot\mathbf{r}}/\mathbf{r} = \frac{1}{\pi^2 \sqrt{2}} \int_0^{\infty} ds\, I_x I_y I_z, \tag{44}$$

where

$$I_x = \int_{-R}^{R} dx e^{-(s^2x^2 - ip_x x)}, \quad I_y = \int_{-R}^{R} dy e^{-(s^2y^2 - ip_y y)}, \quad I_z = \int_{-R}^{R} dz e^{-(s^2z^2 - ip_z z)}.$$

In this representation the inner integrations can be solved analytically

$$I_x = e^{-p_x^2/4s^2} (\pi/s)^{1/2} \operatorname{Re}(1 - e^{-z^2} w(iz)), \tag{45}$$

where now

$$z = (Rs) - i(p_x/(2s)).$$

Unlike Methods 1 and 2 this technique is completely general and its accuracy does not depend on the absence or presence of exchange terms. Of the three methods proposed here, this one will obviously be the method of choice for multiple orbital systems if it can accurately remove the singularity in Eq. (32) and (33).

To test each of these three methods we first calculate the potential energies of the Helium atom using the $1s$-like orbital

$$\phi(p_{klm}) = \text{Norm}/(p_{klm}^2 + 2)^2 \tag{46}$$

and in Table I we compare these results with the exact value. The energies

TABLE I

Components of the Energy of the Helium Atom

	$N^3=32$	$N^3=64$	$N^3=128$	$N^3=256$	$N^3=512$	Extrapolated[a]
Kinetic energy						
P=10	1.987864	1.988989	1.988998	1.989000	-	1.989001(0)
P=20		1.997483	1.998578	1.998578	-	1.998578(0)
P=30			1.999559	1.999576	1.999576	1.999576(0)
P=40			1.998727	1.999821	1.999821	1.999821(0)
Exact						2.000000
Electron-nuclear potential energy						
Method 1						
P=10	2.828310	2.818470	2.816513	2.816110	-	2.815985(1)
P=20		2.835600	2.828280	2.826958	-	2.826625(45)
P=30			2.831765	2.828520	-	2.827438(1082)
P=40			2.835421	2.829390	-	2.827380(2010)
Method 2						
P=10	2.822200	2.817690	2.816417	2.816100	-	2.815990(0)
P=20		2.829490	2.827508	2.826860	-	2.826630(14)
P=30			2.829169	2.828200	-	2.827877(323)
P=40			2.829313	2.828620	-	2.828389(231)
Method 3						
P=10	2.815221	2.815971	2.815986	2.815990	-	2.815991(0)
P=20		2.825953	2.826646	2.826646	-	2.826646(0)
P=30		2.793198	2.827864	2.827875	-	2.827879(4)
P=40			2.827498	2.828189	-	2.828419(230)
Exact						2.828427
Electron-electron potential energy						
Method 1						
P=10	0.893140	0.885490	0.884168	0.883920	-	0.883846(1)
P=20		0.891450	0.885086	0.884086	-	0.883805(52)
P=30			0.887132	0.884370	-	0.883449(921)
P=40			0.890590	0.884870	-	0.882963(1907)
Method 2						
P=10	0.887040	0.884720	0.884072	0.883910	-	0.883856(0)
P=20		0.885340	0.884313	0.883990	-	0.883876(6)
P=30			0.884537	0.884050	-	0.883888(163)
P=40			0.884482	0.884160	-	0.884053(107)
Method 3						
P=10	0.883506	0.883856	0.883856	0.883856	-	0.883856(0)
P=20		0.883533	0.883882	0.883882	-	0.883882(0)
P=30		0.868551	0.883877	0.883883	-	0.883885(2)
P=40			0 883534	0.883883	-	0.883999(116)
Exact						0.883883

[a] The parentheses contain an estimate of the integration error.

Note. Equation (46) is used as the orbital. Values are in hartrees and the potential energies have their signs reversed.

calculated using Methods 1 and 2 show that including second derivatives significantly improves the addition and subtraction of the singularity and that Romberg integration is needed to achieve even modest accuracy. In contrast, however, Method 3 produces results which are much less noisy than either of these other two methods and which converge much faster. Values which were only estimated to be close to the exact integrated limit are now obtainable directly.

In Tables II–V we compare our previous SCF values (Method 2) for the Helium atom, the B^{+3} ion, the H_2 molecule and the H_3^+ ion with the results given by Method 3. We selected this set of two electron calculations because they represent a good series of tests for each method. Even though they contain only one orbital they allow us to examine the behavior of the general algorithm as a function of orbital energy, grid size, and grid density. Like the 1*s* calculations in Table I, Method 3 gives much better results than Method 2. In fact, we now believe that our best value is the $(P=40, N=256^3)$ point rather than the Romberg result for $P=40$ since Romberg integration is somewhat unreliable when only two points are available. With the possible exception of the B^{+3} ion, this point is probably closer to the exact result because the spacing here $(h=0.3125)$ produces a converged numerical integration in the $(P=20, N=128^3)$ calculation. The final SCF values for He (-2.86109), B^{+3} (-21.93381), H_2 (-1.13359), and H_3^+ (-1.30035) are not that much different from the earlier calculations but the convergence is much smoother and thus the integration error is smaller. There is no real change, however, in the integration and truncation errors. A complete discussion of these various error estimates is given in Ref. [4].

In addition to being able to predict the error associated with our energies, it is also important to know if they are variational. Tables II–V show that for a fixed cube size *P*, Method 2 produces upper bounds to the Hartree–Fock limit when an accurate Romberg integration is available although the individual energies are both higher and lower than this result. In contrast, almost all of the individual calculations of Method 3 appear to be upper bounds to the Hartree–Fock limit, Those cases which are not, e.g., the Helium $(P=30, N=64^3)$ SCF calculation, occur when the distance between the points is relatively large. When this distance is reduced, the value becomes more reasonable in appearance. Given an accurate numerical integration, our data also shows that as *P* becomes larger the SCF energy approaches the Hartree–Fock limit monotonically from above. Both of these trends can be understood by comparing them with their LCAO counterparts. In such calculations a variational upper bound exists only if the molecular integrals are computed accurately. In our approach, the number of points, *N*, for a fixed size cube corresponds to the accuracy of these integrals. Thus only when our numerical integration is saturated are our results reliable. Similarly an increase in the size of the integration cube corresponds to an enlargement of the basis set in LCAO–SCF calculations. Just as an increase in the number of basis functions leads to a monotonic decrease in the SCF energy, so an increase in *P* leads to the same result. These trends are not unique to our algorithm—all numerical orbital calculations must exhibit them.

TABLE II

SCF Values for the Helium Atom

	$N=32^3$	$N=64^3$	$N=128^3$	$N=256^3$	Extrapolated[a]
Method 2					
P=10					
Energy	2.85079(0)	2.84309(0)	2.84120(0)	2.84073(0)	2.84057(0)(0)(-)
V/T	2.02177(7)	2.01841(7)	2.01769(7)	2.01751(7)	2.01745(7)(0)(-)
ε	0.91067(2)	0.91085(2)	0.91086(2)	0.91086(2)	0.91086(2)(0)(-)
P=20					
Energy		2.86310(0)	2.85910(0)	2.85813(0)	2.85781(0)(0)(1724)
V/T		2.00572(7)	2.00417(6)	2.00373(7)	2.00358(7)(0)(1387)
ε		0.91690(2)	0.91677(2)	0.91673(2)	0.91672(2)(0)(586)
P=30					
Energy			2.86231(0)	2.86085(8)	2.86036(8)(49)(255)
V/T			2.00213(7)	2.00150(1)	2.00129(7)(21)(229)
ε			0.91760(2)	0.91752(2)	0.91749(2)(6)(77)
P=40					
Energy			2.86380(0)	2.86173(0)	2.86104(0)(69)(68)
V/T			2 00200(7)	2.00082(7)	2.00043(7)(39)(86)
ε			0.91798(2)	0.91779(1)	0.91773(2)(6)(24)
Method 3					
P=10					
Energy	2.84039(0)	2.84051(0)	2.84056(0)	2.84057(0)	2.84057(0)(0)(-)
V/T	2.01803(6)	2.01751(7)	2.01747(7)	2.01746(6)	2.01746(7)(0)(-)
ε	0.91096(2)	0.91084(2)	0.91086(2)	0.91086(2)	0.91086(2)(0)(-)
P=20					
Energy		2.85787(0)	2.85781(0)	2.85781(0)	2.85781(0)(0)(1724)
V/T		2.00386(7)	2.00354(7)	2.00354(7)	2.00354(7)(0)(1392)
ε		0.91690(2)	0.91673(2)	0 91673(2)	0.91673(2)(0)(587)
P=30					
Energy		2.86567(0)	2.86037(0)	2.86037(0)	2.86037(0)(0)(255)
V/T		2.01767(10)	2.00128(7)	2.00127(7)	2.00127(10)(21)(227)
ε		0.92585(3)	0.91756(2)	0.91756(2)	0.91756(3)(0)(83)
P=40					
Energy			2.86115(0)	2.86109(0)	2.86107(0)(2)(70)
V/T			2.00090(8)	2.00050(7)	2.00037(8)(13)(90)
ε			0.91796(2)	0.91779(2)	0.91773(2)(6)(17)
Basis set[b]					
Energy					2.86168
V/T					2.00000
ε					0.91795

[a] The parentheses contain an estimate of the iteration error, the integration error and the truncation error respectively.

[b] Reference 13.

Note. Values are in hartrees with signs reversed.

TABLE III

SCF Values for the Boron^{+3} Ion

	$N=32^3$	$N=64^3$	$N=128^3$	$N=256^3$	Extrapolated[a]
Method 2					
P=10					
Energy	20.87107(0)	20.85776(0)	20.85444(0)	20.85361(0)	20.85332(0)(0)(-)
V/T	2.13358(1)	2.13212(1)	2.13176(1)	2.13167(0)	2.13164(1)(0)(-)
ε	8.98733(2)	8.98918(2)	8.98965(2)	8.98976(2)	8.98980(2)(0)(-)
P=20					
Energy		21.74225(0)	21.73129(0)	21.72855(0)	21.72764(0)(0)(87432)
V/T		2.02701(2)	2.02644(2)	2.02630(2)	2.02625(2)(0)(10539)
ε		9.42516(2)	9.42530(2)	9.42533(2)	9.42534(2)(0)(43554)
P=30					
Energy			21.88728(0)	21.88298(0)	21.88155(0)(143)(15391)
V/T			2.01155(2)	2.01135(2)	2.01128(2)(7)(1497)
ε			9.49615(3)	9.49616(3)	9.49616(3)(0)(7082)
P=40					
Energy			21.94153(0)	21.93575(0)	21.93382(0)(193)(5227)
V/T			2.00633(2)	2.00606(2)	2.00597(2)(9)(531)
ε			9.51924(3)	9.51925(3)	9.51925(3)(0)(2309)
Method 3					
P=10					
Energy	20.84013(0)	20.85002(0)	20.85251(0)	20.85313(0)	20.85334(0)(0)(-)
V/T	2.13273(1)	2.13191(1)	2.13170(1)	2.13165(1)	2.13163(1)(0)(-)
ε	8.98482(2)	8.98855(2)	8.98949(2)	8.98973(3)	8.98981(3)(0)(-)
P=20					
Energy		21.72675(0)	21.72741(0	21.72758(0)	21.72764(0)(0)(12570)
V/T		2.02164(1)	2.02628(2)	2.02626(1)	2.02625(1)(1)(10538)
ε		9.42498(2)	9.42525(2)	9.42532(2)	9.42534(2)(0)(43553)
P=30					
Energy		21.88124(0)	21.88147(0)	21.88152(0)	21.88154(0)(0)(15390)
V/T		2.01132(2)	2.01129(2)	2.01128(0)	2.01128(0)(0)(1497)
ε		9.49603(3)	9.49613(3)	9.49615(3)	9.49616(3)(0)(7082)
P=40					
Energy			21.93378(0)	21.93381(0)	21.93382(0)(1)(5228)
V/T			2.00598(2)	2.00597(2)	2.00597(2)(0)(531)
ε			9.51924(3)	9.51925(2)	9.51925(2)(0)(2309)
Basis set[b]					
Energy					21.98623
V/T					2.00000
ε					9.54194

[a] The parentheses contain an estimate of the iteration error, the integration error and the truncation error respectively.

[b] Reference 13.

Note. Values are in hartrees with signs reversed.

TABLE IV

SCF Values for the Molecule H_2 ($R = 1.4$ au)

	$N=32^3$	$N=64^3$	$N=128^3$	$N=256^3$	Extrapolated[a]
Method 2					
P=10					
Energy	1.14379(0)	1.13431(0)	1.13237(0)	1.13189(0)	1.13173(0)(0)(-)
V/T	2.02838(103)	2.01190(80)	2.01016(80)	2.00972(80)	2.00957(103)(0)(-)
ε	0.59595(33)	0.59385(28)	0.59385(27)	0.59385(27)	0.59385(33)(0)(-)
P=20					
Energy		1.14021(0)	1.13458(0)	1.13360(0)	1.13331(0)(4)(158)
V/T		2.02129(105)	2.00853(7)	2.00758(81)	2.00746(105)(20)(211)
ε		0.59651(33)	0.59453(7)	0.59440(27)	0.59439(33)(3)(54)
P=30					
Energy			1.13558(0)	1.13401(0)	1.13349(0)(52)(18)
V/T			2.00903(84)	2.00729(81)	2.00671(84)(58)(75)
ε			0.59458(28)	0.59449(27)	0.59446(28)(3)(7)
P=40					
Energy			1.13793(0)	1.13424(0)	1.13301(0)(123)(48)
V/T			2.01840(105)	2.00731(80)	2.00361(105)(370)(310)
ε			0.59661(33)	0.59451(27)	0.59381(33)(70)(65)
Method 3					
P=10					
Energy	1.13287(0)	1.13172(0)	1.13173(0)	1.13173(0)	1.13173(0)(0)(-)
V/T	2.01807(100)	2.00960(80)	2.00958(80)	2.00958(80)	2.00958(100)(0)(-)
ε	0.59588(33)	0.59385(28)	0.59385(28)	0.59385(27)	0.59385(33)(0)(-)
P=20					
Energy		1.13445(0)	1.13328(0)	1.13328(0)	1.13328(0)(0)(155)
V/T		2.01563(102)	2.00729(81)	2.00729(81)	2.00729(102)(0)(229)
ε		0.59644(33)	0.59441(28)	0.59441(28)	0.59441(33)(0)(56)
P=30					
Energy		1.16647(0)	1.13356(0)	1.13352(0)	1.13350(0)(1)(22)
V/T		2.16985(208)	2.00722(84)	2.00686(82)	2.00674(208)(12)(55)
ε		0.62610(42)	0.59459(28)	0.59449(27)	0.59446(28)(3)(5)
P=40					
Energy			1.13476(0)	1.13359(0)	1.13320(0)(39)(30)
V/T			2.01506(102)	2.00674(82)	2.00397(102)(277)(277)
ε			0.59654(33)	0.59451(27)	0.59383(33)(68)(63)
Basis set[b]					
Energy					1.13363
V/T					-
ε					0.59466

[a] The parentheses contain an estimate of the iteration error, the integration error and the truncation error respectively.

[b] Reference 14, orbital energy from reference 3b.

Note. Values are in hartrees with signs reversed

TABLE V

SCF Values for the Molecule H_3^+

	$N=32^3$	$N=64^3$	$N=128^3$	$N=256^3$	Extrapolated[a]
Method 2					
P=10	-				
Energy	1.31458(0)	1.30112(0)	1.29789(0)	1.29708(0)	1.29681(0)(0)(-)
V/T	2.02012(42)	2.00875(41)	2.00623(41)	2.00602(129)	2.00600(129)(1)(-)
ε	1.21074(16)	1.21051(16)	1.21051(16)	1.21051(16)	1.21051(16)(0)(-)
P=20					
Energy		1.30923(0)	1.30220(0)	1.30058(0)	1.30005(0)(1)(324)
V/T		2.00952(45)	2.00323(44)	2.00198(44)	2.00159(45)(3)(441)
ε		1.21211(17)	1.21188(16)	1.21187(16)	1.21187(17)(0)(136)
P=30					
Energy			1.30358(0)	1.30108(1)	1.30025(1)(83)(20)
V/T			2.00388(44)	2.00239(129)	2.00189(129)(50)(30)
ε			1.21198(17)	1.21197(17)	1.21197(17)(0)(10)
P=40					
Energy			1.30524(0)	1.30143(0)	1.30016(0)(127)(9)
V/T			2.00587(45)	2.00251(129)	2.00139(129)(112)(50)
ε			1.21224(17)	1.21201(16)	1.21193(17)(8)(5)
Method 3					
P=10					
Energy	1.29692(0)	1.29680(0)	1.29681(0)	1.29681(0)	1.29681(0)(0)(-)
V/T	2.00640(41)	2.00541(41)	2.00540(41)	2.00540(40)	2.00540(41)(0)(-)
ε	1.21072(16)	1.21051(16)	1.21051(16)	1.21051(16)	1.21051(16)(0)(-)
P=20					
Energy		1.30018(0)	1.30004(0)	1.30004(0)	1.30004(0)(0)(323)
V/T		2.00253(45)	2.00157(43)	2.00157(43)	2.00157(45)(0)(383)
ε		1.21210(16)	1.21187(17)	1.21187(17)	1.21187(17)(0)(136)
P=30					
Energy		1.31472(0)	1.30027(0)	1.30027(0)	1.30027(0)(0)(23)
V/T		2.06617(69)	2.00134(44)	2.00133(44)	2.00133(69)(0)(24)
ε		1.22612(23)	1.21197(17)	1.21197(17)	1.21197(23)(0)(10)
P=40					
Energy			1.30049(0)	1.30035(0)	1.30030(0)(5)(3)
V/T			2.00219(45)	2.00123(44)	2.00091(45)(3)(42)
ε			1.21223(16)	1.21200(17)	1.21192(17)(8)(5)
Basis set[b]					
Energy					1.30032
V/T					2.00029
ε					1.21166

[a] The parentheses contain an estimate of the iteration error, the integration error and the truncation error respectively.

[b] Reference 15, energy from reference 12.

Note. The geometry of the molecule is an equilateral triangle with $R = 1.6405$ au. Values are in hartrees with signs reversed.

4. REDUCING THE TRUNCATION ERROR

With the success of our improved treatment of the Coulomb singularity and its effect on the integration error the greatest impediment to increased accuracy is now the truncation error. One way of reducing this problem is simply to increase the size of the integration cube, but to maintain an accurate numerical integration this necessitates a corresponding increase in the number of points. Since each doubling of the total number of points slows the program down by roughly an order of magnitude, this idea becomes quickly unmanageable. An alternative is to use our finite cube results to extrapolate to the infinite cube value. To do so, however, requires an understanding of the behavior of a molecular orbital when the momentum is large. Work by Lassettre [10] and others [7, 11] has shown that in such a limit the molecular orbital has the form

$$\phi_\alpha(\mathbf{p}) \sim (p^2 + 2\varepsilon_\alpha)^{-2} \sum_{a=1}^{\#\text{Atoms}} c_{a,\alpha}(\mathbf{p})\, e^{i\mathbf{p}\cdot\mathbf{R}_a}, \tag{47}$$

TABLE VI

Extrapolation of SCF Energies to
Reduce Truncation Error Using Finite Cube Results
Fit to Eq. (48) and (49)

System	Two parameters[a]		Three parameters[a]		Extrapolated Estimate[b]
He	30,40	2.8616135	20,30,40	2.8616508	2.86165(2)
	20,30	2.8614433	10,20,30	2.8616291	
		---------		---------	
		1702		217	
B^{+3}	30,40	21.9719609	20,30,40	21.9775748	21.97757(2436)
	20,30	21.9463395	10,20,30	21.9532102	
		----------		----------	
		256214		243646	
H_2	30,40	1.1336359	20,30,40	1.1336386	1.13364(6)
	20,30	1.1336237	10,20,30	1.1336328	
		---------		---------	
		122		58	
H_3^+	30,40	1.3004060	20,30,40	1.3004150	1.30041(4)
	20,30	1.3003630	10,20,30	1.3003520	
		---------		---------	
		430		630	

[a] These calculations are performed using the $N=256^3$ energies.

[b] The parenthesis contains the new estimate of the truncation error.

Note. Values are in hartrees with signs reversed.

where

$$c_{a,\alpha}(\mathbf{p}) > 0 \text{ and bounded.}$$

Approximating this function as simply p^{-4}, it is easy to show that the kinetic energy and hence the total SCF energy must decay like p^{-3}. By least square fitting our finite cube values to formulas of the form

$$E_{\mathrm{SCF}} \sim a + b/p^3 \tag{48}$$

$$E_{\mathrm{SCF}} \sim a + b/p^3 + c/p^5 \tag{49}$$

the constant "a" can be used as an estimate of the infinite cube result. Furthermore, when various cube sizes are used to produce this estimate it is possible to estimate the error in this extrapolation. In Table VI we present the results of such calculations for our four examples. To determine whether Eq. (48) or (49) is more accurate we compare each calculation with a similar one which was performed on a smaller cube (e.g., $P = 30$, $P = 40$ and $P = 20$, $P = 30$). The difference in these two values is itself an estimate of the truncation error so we take whichever error is smaller. All of these calculations are done using the $N = 256^3$ energies to minimize any effect from the integration error. Since our extrapolated values and their errors agree with the accepted values for the three most accurately known examples (the Helium atom, the B^{+3} ion, and the H_2 molecule) we believe that the same is also true of the H_3^+ ion.

5. CONCLUSIONS

We have shown that a simple modification to our original algorithm significantly improves the numerical treatment of the Coulomb singularity. This change not only accelerates the convergence of the numerical integration but has several computational features which make it attractive. Unlike the previous method the point $p = 0$ need no longer be treated as a special case and no numerical derivatives need be taken. Both of these requirements inhibited vectorization. We have also argued that in the limit of an accurate integration our result should be variational even for a finite size cube and that our biggest remaining problem, truncation error, can be decreased by a simple extrapolation. Because of these improvements, our best SCF energy for H_3^+ is now confidently reported as -1.30035 hartrees. This value is lower than any published basis set calculation. The closest value in the literature is a calculation by King and Morokuma [12] (-1.30032 hartrees) which uses 69 GTOs. A comparison of this and other basis set calculations with our result is given in Table VII. King and Morokuma estimate that the Hartree–Fock limit for this system is about -1.30036 hartrees. Although they do not give the error associated with this estimate, it is in good agreement with our extrapolated value of

TABLE VII

Comparison of SCF Values for the Molecule H_3^+

DZ/S basis	-1.27555	6 contracted GTOs.[a]
631G** basis	-1.29852	18 contracted GTOs.[b]
5S 2P basis	-1.29971	33 contracted GTOs.[c]
5S basis	-1.29993	5 optimized GTOs vith D3h symmetry.[d]
(7,3,1/3) basis	-1.30032	69 uncontracted GTOs.[e]
This work	-1.30035	1 numerical orbital vith no symmetry.
This work	-1.30041	extrapolated result from Table 6.

[a] Basis set from Ref. 16.

[b] Basis set from Ref. 17.

[c] Basis set from Ref. 18.

[d] Calculation described in Ref. 15.

[e] Calculation described in Ref. 12.

Note. The geometry of the molecule is an equilateral triangle with $R = 1.6405$ au. Values are in hartrees.

$-1.30041(4)$ hartrees. These energies show conclusively that very accurate SCF calculations on polyatomics are possible with numerical orbitals. Future improvements to our algorithm can only make this method more attractive.

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REFERENCES

1. Two excellent reviews of the LCAO problem have been given by S. WILSON, *Methods in Computational Molecular Physics*, edited by G. H F. Diercksen and S. Wilson (Reidel, Dordrecht, 1983) and by E. R Davidson and D. Feller, *Chem. Rev.* **86**, 681 (1986).
2 C. FROESE FISCHER, *The Hartree–Fock Method for Atoms* (Wiley, New York, 1977) and references therein.

3. See, for example, E. A. McCullough, Jr., *Comput. Phys. Rep.* **4**, 265 (1986); L. Laaksonen, P. Pyykko, and D. Sundholm, *Comput. Phys. Rep.* **4**, 315 (1986).
4. S. A. Alexander and H. J. Monkhorst, *Int. J. Quantum Chem.* **32**, 361 (1987).
5. H. J. Monkhorst and B. Jeziorski, *J. Chem. Phys.* **71**, 5268 (1979).
6. J. Navaza and G. Tsoucaris, *Phys. Rev. A* **24**, 683 (1981); M. Defranceschi, M. Suard, and G. Berthier, *C. R.* **299**, 9 (1984); M. Defranceschi, M Suard, and G. Berthier, *Int. J Quantum Chem.* **25**, 863 (1984); G. Berthier, M. Defranceschi, J. Navaza, M. Suard, and G. Tsoucaris, *Theochem* **120**, 343 (1985).
7. H. J. Monkhorst, unpublished notes.
8. W. Gautschi,, *SIAM J. Numer. Anal.* **7**, 187 (1970).
9. R L Coldwell, *Phys. Rev. D* **5**, 1273 (1972).
10 E N Lassettre, *J. Chem. Phys.* **43**, 4497 (1965); **57**, 4357 (1972); **70**, 3468 (1979); **72**, 2374 (1980); **74**, 1225 (1981).
11. C L. Davis, H J. A Jensen, and H. J. Monkhorst, *J. Chem. Phys.* **80**, 840 (1984).
12 H. F. King and K. Morokuma, *J. Chem. Phys.* **71**, 3213 (1979).
13. C C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).
14. W. Kolos and C C. J. Roothaan, *Rev. Mod. Phys.* **32**, 219 (1960).
15. M. E Schwartz and L. J. Schaad, *J. Chem. Phys.* **47**, 5325 (1967).
16. T H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).
17. P. C. Hariharan and J A Pople, *Theor. Chim. Acta* **28**, 213 (1973)
18. G. C. Lie and E. Clementi, *J. Chem. Phys.* **60**, 1275 (1974).