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Application of Cholesky-Like Matrix Decomposition Methods to the Evaluation of Atomic Orbital Integrals and Integral Derivatives

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Abstract

When viewed as a square two-indexed matrix, the array of atomic orbital based, two-electron integrals $(ij|kl)$ is a positive semidefinite array. Beebe and Linderberg showed, in 1977, that actual or near linear dependencies often exist within the types of atomic orbital basis sets employed in conventional quantum chemical calculations. In fact, large (i.e., higher quality) bases were shown to be substantially more redundant than smaller or more spatially separated bases. In situations where there exists significant basis near redundancy, the rank (r) of the $(ij|kl) = V_{I,J}$ matrix of integrals will be significantly smaller than the matrix dimension M.

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The idea of using the Cholesky procedure for generating two-electron integrals was put forth by Beebe and Linderberg in 1977[1]. Linear dependencies caused by either basis set redundance or symmetry give the matrix (ij|kl) a true rank (r) smaller than the apparent rank (i.e., its dimension M). In applying the method to integral derivatives as described in Section Ia, additional dependencies can arise. The geometrical derivative of an integral involving Gaussian-type orbitals (GTO's) can be expressed as a difference between integrals over GTO's with angular momentum quantum numbers one higher and one lower than that of the differentiated GTO. Thus, if a very flexible basis set is used, one might reasonably expect that many of the integral derivatives (i.e., those involving GTO's with smaller angular momentum) could be reexpressed as linear combinations of two-electron integrals themselves, in which case redundancy would occur in the combined list of integrals and integral derivatives.

In the next two subsections we describe how we implement the decomposition of the integral and integral derivative array and how we have computed those subsets of integrals and integral derivatives that the Cholesky algorithm requires. In Section II we present and analyze the results of our calculations on C_2 and on benzene.

Ia. Procedure

Consider the atomic orbital basis $\{\phi_k(r)\}$, $(k=1,\ldots,N)$ where N is the number of basis functions. The two-electron integrals form a matrix $\underline{V}$ defined as

$$V_{IJ} = V_{ij,kl} = (ij|kl)$$
$$= \iint \phi_i^*(1)\phi_j(1) \frac{1}{r_{12}} \phi_k^*(2)\phi_l(2)\, dr_1 dr_2 \qquad (1)$$

To simplify notation, we use a capital index to denote the two indices occurring in the orbital products $I=ij$, $J=kl$. The range of I and J is then from 1 to M where $M = N(N+1)/2$.

The matrix of two-electron integrals is clearly positive semi-definite as $1/r_{12}$ is a positive definite weighting factor with the volume elements $(dr_1 dr_2)$. It can be decomposed via the Cholesky algorithm to form a lower triangular matrix $\underline{L}$ such that

$$\underline{V} = \underline{L}\underline{L}^T \qquad (2)$$

As long as $\underline{V}$ is positive definite, $\underline{L}$ always exists, and it has been shown that the Cholesky algorithm is numerically stable.[2]

The algorithm utilized to decompose $\underline{V}$ into $\underline{L}\underline{L}^T$ can be detailed as follows. For $J=1,2,\ldots,M$, we compute

$$L_{J,J} = \left[V_{J,J} - \sum_{k=1}^{J-1} L_{J,k}^2 \right]^{1/2} \qquad (3.1)$$

and, for each J, we evaluate

$$L_{I,J} = \left[V_{I,J} - \sum_{k=1}^{J-1} L_{I,k} L_{J,k} \right] \frac{1}{L_{J,J}}, \text{ for } I=J+1,\ldots,M \qquad (3.2)$$

If carried through to completion, in which case $\underline{L}$ would have the same dimension as $\underline{V}$ itself, this process would require the evaluation of M square roots, $M(M-1)(M-4)/6$ multiplications or divisions, and $M(M-1)(M+2)/6$ additions or subtractions. It would also necessitate the calculation of each of the elements of the original $\underline{V}$ array, and would therefore not produce any savings. In fact, since $M=N(N+1)/2$, this process, if carried to completion, leads to on the order of $N^6/12$ arithmetic steps, in which case the <u>decomposition</u> of $\underline{V}$ into $\underline{L}$ would be more time consuming than the evaluation of the full $\underline{V}$ matrix by conventional means.

The key to implementing the above algorithm in a manner which <u>can</u> overcome this N^6 dependence lies in processing the matrix elements in a way which allows the (potential) reduced rank of $\underline{V}$ to be exploited. We emphasize that it is the physical content (i.e., near redundancy and saturation) of the basis, which gives rise to the rank reduction and allows the process we describe here to succeed, rather than the process itself. To perform the Cholesky decomposition in an order which exploits rank reduction, we proceed as follows:

1) We first calculate all of the <u>diagonal</u> <u>elements</u> $V_{J,J}$ using conventional integral evaluation methods, and we sort these diagonal $V_{J,J}$ into a non-increasing order, keeping a record of the original order.
2) For $J = 1,2,\ldots M$, we set $L_{J,J} = V^{1/2}_{J,J}$, and we then (for each J)
3) calculate the column of integrals $V_{I,J}$, for $I = J+1,\ldots,M$ using conventional means.
4) We then (for each J) set $L_{I,J} = \left[V_{I,J} - \sum_{k=1}^{J-1} L_{I,k} L_{J,k}\right] \frac{1}{L_{J,J}}$, for $I = J+1,\ldots,M$.
5) Finally, we modify the diagonal elements according to $V_{I,I} = V_{I,I} - L^2_{I,J}$, $I = J+1,\ldots,M$.

This is equivalent to the procedure given in equations 3.1 and 3.2. However, at any point in the calculation (say the J^{th} step), $V_{J,J}$ is the largest remaining element in the matrix $\underline{V}$. If the matrix elements are known or needed only to a given numerical accuracy δ, then when $V_{J,J} \leq \delta$ the calculation can be stopped with no numerical loss. If the decomposition is stopped at point J, then in the reformation of the $\underline{V}$ matrix as $\underline{LL}^T$, all elements formed in steps 1 to J are exact (to machine precision), and elements formed in steps J+1 to M are in error by less than δ. Clearly the key question is whether, for reasonable values of δ (e.g., $\delta \sim 10^{-9}$), the decomposition process can be stopped (at J=r) early enough to make this decomposition less time consuming than the evaluation of the full matrix by conventional means. The process itself will <u>not</u> succeed unless, for a given cutoff δ, the rank r of $\underline{V}$ grows slower than the dimension M of $\underline{V}$; that is, the (near) redundancy in the basis function space is what can make the process succeed.

In expanding the method to include first integral derivatives, the matrix $\underline{V}$ is redefined, but the machinery of the decomposition given above is unchanged. When dealing with the integrals, a row (or column) of $\underline{V}$ is labeled by the functions $\{f_{ij}\} = \{\phi_i^*(1)\phi_j(1),\ i = 1,N;\ j = 1,\ i\}$. To include the integral derivative case, this set of functions is expanded to be $\{f_{ij}\} = \{\phi_i^*(1)\phi_j(1), \frac{d}{dx}(\phi_i^*(1)\phi_j(1))\}$, where x labels the atomic displacements whose integral derivatives are to be included. If the derivative function is zero, the corresponding f_{ij} is deleted from the set.

Ib. Integral Evaluation Methods

As was stated before, the Cholesky decomposition takes advantage of (near) redundancies in the matrix of two-electron integrals. The manner of formation of the integrals or even the type of integrals does not enter directly into the procedure. Gaussian-type orbitals were chosen in this implementation. For a GTO, the ϕ's in eq 1 takes the form

$$\phi(l,m,n,\alpha,R) = (x-X)^{l}(y-Y)^{m}(z-Z)^{n}\, e^{-\alpha R^{2}}.$$

The use of GTO's is widespread in quantum chemical calculations because of the relative ease with which electron repulsion integrals can be calculated compared with other basis set types such as Slater-type orbitals.

The Rys polynomial method of two electron integral and integral derivative evaluation is used.[3] This method was chosen because of the ease and efficiency with which integrals over high angular momentum functions can be calculated. In this method, a Gaussian transform of the Coulomb operator in eq 1 is performed

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \exp(-u^2 r_{12}^2)\, du. \tag{4}$$

This allows a separation of variables for the three cartesian coordinates so that the two electron integral can be rewritten as

$$(ij|kl) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} I'_x(u) I'_y(u) I'_z(u)\, du. \tag{5}$$

I'_x, I'_y, and I'_z are two-dimensional integrals over the respective cartesian coordinates of the two electrons. With a change of variables

$$t^2 = u^2/\,(\rho+u^2) \tag{6.1}$$

$$I_x = 1/\sqrt{1-t^2 I'_x} \tag{6.2}$$

$$\rho = (\alpha+\beta)(\gamma+\delta)/(\alpha+\beta+\gamma+\delta) \tag{6.3}$$

the two-electron integral takes the form

$$(ij|kl) = 2\sqrt{\frac{\rho}{\pi}} \int_0^1 I_x(t) I_y(t) I_z(t)\, dt$$

$$= \int_0^1 P_L(t)\, e^{-\rho PQ^2 t^2} dt \tag{7}$$

where $P_L(t)$ is an L^{th} degree polynomial in t^2, $L=l_i+l_j+l_k+l_l$, and P and Q are functions of the Gaussian exponents and positions.

When one differentiates the expression in eq 7 with respect to position on one nucleus, the derivative passes through the integral. The integrand is then an L+1th polynomial in t^2 and may be evaluated using the Rys quadrature.

$$\begin{aligned}\frac{\partial(ij|kl)}{\partial X_a} &= 2\sqrt{\frac{\rho}{\pi}} \int_0^1 \frac{\partial I_x(t)}{\partial X_a}\, I_y(t)\, I_z(t)\, \partial t \\ &= \int_0^1 P'_{L+1}(t)\, e^{-\rho PQ^2 t^2}\, \partial t \\ &= \sum_{\alpha=1}^{n'} \frac{\partial I_x(t_\alpha)}{\partial X_a}\, I_y(t_\alpha)\, I_z(t_\alpha)\, W^*_\alpha\,, \quad n' > \frac{L+1}{2} \qquad (8)\end{aligned}$$

The recursion relationship given in reference 3c has been differentiated to give the quantity $\frac{\partial I_x(t_\alpha)}{\partial X_a}$ directly.

The integral derivative could have been expressed as a difference of integrals over higher and lower angular momentum functions, but, as Pulay has pointed out[4], the relative efficiency of the two methods is questionable. The current implementation was judged to be more easily computer coded and was chosen for that reason.

II. Results

IIa. The Test Calculations

As the major test of this procedure, a series of calculations was done on diatomic carbon with twenty-two separate, fully uncontracted, even-tempered basis sets varying in size from ten (2s1p) to seventy-two (18s6p) functions. This large range of basis sizes was studied to explore the effects of increasing basis near redundancy.

In each test calculation, the Cholesky decomposition was allowed to proceed to tolerance (δ) of zero. As the process advanced, intermediate rank reduction information (i.e. r as a function of δ) and CPU timing data were saved. This was done first on the list of two-electron integrals and then for the list of integrals and integral derivatives (with respect to the C-C bond length coordinate). Tables 1-4 summarize the rank reduction data realized in these calculations at δ tolerance values of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} (in most quantum chemistry codes, integrals and integral derivatives are computed to precision of approximately 10^{-11} au). Graphical representations of this data are shown in figures 1-4.

All calculations shown here were done on our FPS-164 array processor but did not make use of its matrix accelerator (MAX) board. For the purposes of testing the Cholesky algorithm, all integrals which were not zero by symmetry were explicitly calculated although this should not be necessary in production runs.

IIb. Analysis of Findings

As the data of Tables 1 and 2 show, the rank r of the matrices is much smaller than the dimension M even for tight cutoff tolerances and increases slowly as the dimension increases. As M continues to increase, the rank seems to approach an asymptotic value (see figs 3 and 4) after which addition of basis functions does not increase the rank. At this point, the basis set is complete to within the cutoff tolerance. To analyze the potential CPU and/or storage advantages of the Cholesky process applied to the integrals and integral derivatives, we wanted to fit the "data" obtained in our calculations to a reasonable functional form.

In choosing a functional form to fit the M dependence of r, we required the function have an asymptotic limit as the above analysis indicates and a slope of approximately one for small values of M because $r \rightarrow M$ in this limit. We therefore model the variation of r with M as $\alpha\tanh(\beta M^{\gamma})$. For this function, the asymptotic (as $M \rightarrow \infty$) limit is α and, if the optimal value of β is approximately $1/\alpha$, the slope is approximately one for small M.

Results of least squares fits of the above functional form to our r(M) "data" for the two-electron integrals for diatomic carbon are given in table 5 and for two-electron integrals and derivatives in table 6 for the five cutoff tolerances examined. Figures 5 and 6 show the resulting optimal leasts squares curves for the two-electron integrals and for the integrals and derivatives respectively. In the two-electron integral case, the α values range from 186 to 1012 with β values between 0.01140 and 0.00066 and γ vaues between 1.063 and 1.761. For the two-electron integrals and derivatives, α ranges from 326 to 1324, β from 0.01304 to 0.00110, and γ from 1.028 to 1.617. One notes here that the values of β are approximately $1/\alpha$ for each case, satisfying the initial slope requirement (i.e., the fit to the actual "data" is quite good as $M \rightarrow 0$). The result that α values are less than 2500 is of crucial importance as we now illustrate (corresponding to basis set sizes near 50 because $M \cong N^2$).

IIc. Potential Numerical Advantage of the Method

Analysis of the algorithm described in Section Ia. shows that the Cholesky decomposition process requires: (1) arithmetic operations (additions or multiplications) whose numbers scale as (3M-2r+1)(r-1)r/3 as M (and r) increases and (2) integral or integral derivative evaluations whose number varies as Mr - r(r-1)/2. In contrast, the conventional treatment requires M(M+1)/2 integrals to be evaluated. If the CPU time required for a floating point addition or multiplication is denoted A and the (average) time required to evaluate a single two-electron integral or derivative is denoted B, the ratio of the Cholesky to conventional computer time requirements should vary as

$$C/T = \frac{A(3M-2r+1)(r-1)r/3 + B(Mr-r(r-1)/2)}{BM(M+1)/2}$$

This ratio must be less than one for the Cholesky process to be computationally advantageous. On our FPS-164 array processor using non-vectorized code, a floating point multiplication takes 0.540 μsec (with an addition being a factor of three less) and a two-electron integral or integral derivative evaluation requires 503 μsec using the highly optimized ARGOS integral evaluation program[6]. Thus for the following analysis, we set A=0.540 and B=503.

Figures 7 and 8 show C/T for the diatomic carbon data for integrals and integral plus derivatives respectively. For the integrals, the ratio C/T is less than one for all but the tightest cutoff tolerance and is a decreasing function of M as M increases. For the integrals and derivatives, the result is more pronounced with C/T being less than 0.4 for all values of M and decreasing to below 0.1 for $M \geq 1000$. Thus, the Cholesky decomposition process shows much promise for decreasing computation times for integral and (especially) integral and derivative evaluation.

Disk storage requirements may also be greatly reduced by the Cholesky process. The conventional algorithms store on the order of M^2 integrals. The Cholesky algorithm described in Section Ia stores $M(r+1) - r(r+1)/2$ integrals. The ratio of the Cholesky to conventional storage requirements is less than unity for all M and, for large M (as r approaches its asymptotic constant α) decreases as α/M. Saving substantially on storage also leads to increased program performance through reduced I/O. With large main memories characteristic of modern computers, it is possible that all of the requisite integrals can be kept in the high-speed memory of the machine.

In addition to savings in integral evaluation time and storage, the Cholesky process, if advantageous, can give major savings when atomic orbital based, two-electron integrals (ij|kl) must be transformed to the molecular orbital (MO) basis. Because each integral (those given exactly and those approximately) is expressed in the Cholesky procedure as $V_{I,J} = \sum_{k=1}^{r} L_{I,k} L_{k,J}$, the transformation of the I and J indices to the mo basis set can be realized by transforming the first (I) index of the $\{L_{I,k}\}$ array to the mo basis:

$$\sum_{ij} L_{ij,k} C_{ia} C_{jb} = L_{ab,k} = L_{A,k} \tag{9}$$

where the $\{C_{ia}\}$ are the LCAO-MO expansion coefficients. This two-index transformation would be carried out for all $k=1,\ldots,r$, but the k index itself <u>need</u> <u>not</u> be transformed. Thus, the requisite transformation process involves $rN(N+1)$ steps to obtain $\{V_{Ak}\}$; the conventional transformation of V_{IJ} to V_{AB} requires $4N^5$ steps.

IId. Other Tests

As a check on the generality of our findings on C_2 using the above bases, two other sets of calculations were performed with substantially different basis sets. A Dunning 10s6p primitive set[7] and an uncontracted 6-311G set[8] (11s5p primitives) were used for both integral and integral plus integral derivative calculations. Table 7 summarizes the results for these calculations. Comparing these results with those using similarly sized even-tempered basis sets shows that the results are very similar. We therefore feel it is likely that integral and derivative evaluations within any reasonably well optimized moderate to large size basis set will benefit from the Cholesky decomposition.

An additional calculation was done on the benzene molecule to judge the performance of the Cholesky decomposition on a polyatomic system for which many integrals vanish due to large spatial separation between atomic centers and for which basis set saturation was <u>not</u> anticipated. The 36 function STO-3G basis of Hehre, Stewart, and Pople[9] was used in this calculation and the integral derivatives were taken with respect to one C-C bond distance. Although the rank reduction is still significant, the results (Table 8) show a marked decline in the advantage of the Cholesky process. This is primarily due to the smaller basis set size and large spatial separations among the orbitals in the molecule. With this much less flexible basis, there will be fewer near dependencies in the basis, and the Cholesky process is not advantageous.

III. Summary

The Cholesky decomposition method has been shown to be effective in reducing the number of integrals and integral derivatives that need to be calculated, stored, and transformed to the molecular orbital basis for atomic orbital basis sets which contain substantial near redundancy. The saturation of the atomic orbital basis, not the Cholesky process itself, causes this procedure to succeed. As analytical energy and wavefunction derivative methods are applied to larger molecular systems, the number of requisite integrals and integral derivatives grow very rapidly. The incorporation of our method into existing analytical derivative program suites should therefore allow CPU and disk storage requirements to grow at a much slower pace and thereby allow calculations on much larger systems than is thought currently practical.

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Table 1 Rank reduction at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for C_2 two-electron integrals.

basis set	# basis functions	full rank	rank at 10**-3	rank at 10**-6	rank at 10**-9	rank at 10**-12	rank at 10**-15
2s1p	10	55	25	31	32	32	32
3s1p	12	78	30	45	46	46	46
4s1p	14	105	34	60	63	64	64
5s1p	16	136	37	72	80	81	82
5s2p	22	253	60	106	134	166	145
6s2p	24	300	58	123	165	174	179
7s2p	26	351	64	133	185	198	208
8s2p	28	406	66	138	196	214	232
8s3p	34	595	87	170	257	308	328
9s3p	36	666	91	182	278	334	360
10s3p	38	741	91	187	288	353	396
11s3p	40	820	98	194	295	385	424
11s4p	46	1081	111	230	356	472	541
12s4p	48	1176	116	234	360	481	558
13s4p	50	1275	115	240	364	491	564
14s4p	52	1378	114	244	375	505	603
14s5p	58	1711	130	276	422	580	684
15s5p	60	1830	131	275	423	585	732
16s5p	62	1953	134	280	432	598	739
17s5p	64	2080	134	285	448	603	766
17s6p	70	2485	148	319	481	670	850
18s6p	72	2628	149	324	495	674	863

Table 2 Rank reduction at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for C_2 two-electron integrals and derivatives.

basis set	# basis functions	full rank[a]	rank at 10**-3	rank at 10**-6	rank at 10**-9	rank at 10**-12	rank at 10**-15
2s1p	10	110	47	54	55	55	55
3s1p	12	156	58	77	79	79	79
4s1p	14	210	67	99	103	104	104
5s1p	16	272	69	112	122	124	125,
5s2p	22	506	104	159	188	222	203
6s2p	24	600	103	181	227	237	243
7s2p	26	702	111	195	251	265	276
8s2p	28	812	114	203	264	284	303
8s3p	34	1190	156	258	356	408	430
9s3p	36	1332	156	269	373	433	461
10s3p	38	1482	157	280	390	459	503
11s3p	40	1640	169	287	399	492	534
11s4p	46	2162	202	361	500	619	690
12s4p	48	2352	203	358	496	624	702
13s4p	50	2550	201	355	493	627	701
14s4p	52	2756	205	363	511	645	747
14s5p	58	3422	223	407	574	738	850
15s5p	60	3660	235	415	585	755	908
16s5p	62	3906	236	418	593	767	913
17s5p	64	4160	226	420	610	770	937
17s6p	70	4970	255	477	669	867	1058
18s6p	72	5256	258	482	685	872	1070

[a] includes orbital products $\{\phi_i\phi_j\}$ and derivatives $\{\frac{d}{dR}\phi_i\phi_j\}$

Table 3 Fraction of apparent rank at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for C_2 two-electron integrals.

basis set	# basis functions	full rank	frac.of rank at 10**-3	frac.of rank at 10**-6	frac.of rank at 10**-9	frac.of rank at 10**-12	frac.of rank at 10**-15
2s1p	10	55	0.45454	0.56363	0.58181	0.58181	0.58181
3s1p	12	78	0.38461	0.57692	0.58974	0.58974	0.58974
4s1p	14	105	0.32381	0.57142	0.60000	0.60952	0.60952
5s1p	16	136	0.27205	0.52941	0.58823	0.59558	0.60294
5s2p	22	253	0.23715	0.41897	0.52964	0.65612	0.57312
6s2p	24	300	0.19333	0.41000	0.55000	0.58000	0.59666
7s2p	26	351	0.18233	0.37891	0.52706	0.56410	0.59259
8s2p	28	406	0.16256	0.33990	0.48275	0.52709	0.57142
8s3p	34	595	0.14621	0.28571	0.43193	0.51764	0.55126
9s3p	36	666	0.13663	0.27327	0.41741	0.50150	0.54054
10s3p	38	741	0.12280	0.25236	0.38866	0.47638	0.53441
11s3p	40	820	0.11951	0.23658	0.35975	0.46951	0.51707
11s4p	46	1081	0.10268	0.21276	0.32932	0.43663	0.50046
12s4p	48	1176	0.09863	0.19898	0.30612	0.40901	0.47449
13s4p	50	1275	0.09019	0.18823	0.28549	0.38509	0.44235
14s4p	52	1378	0.08272	0.17706	0.27213	0.36647	0.43759
14s5p	58	1711	0.07597	0.16130	0.24663	0.33898	0.39976
15s5p	60	1830	0.07158	0.15027	0.23114	0.31967	0.40000
16s5p	62	1953	0.06861	0.14336	0.22119	0.30619	0.37839
17s5p	64	2080	0.06442	0.13701	0.21538	0.28990	0.36826
17s6p	70	2485	0.05955	0.12837	0.19356	0.26961	0.34205
18s6p	72	2628	0.05669	0.12328	0.18835	0.25646	0.32838

Table 4 Fraction of apparent rank at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for C_2 two-electron integrals and derivatives.

basis set	# basis functions	full rank[a]	frac.of rank at 10**-3	frac.of rank at 10**-6	frac.of rank at 10**-9	frac.of rank at 10**-12	frac.of rank at 10**-15
2s1p	10	110	0.42727	0.49091	0.50000	0.50000	0.50000
3s1p	12	156	0.37179	0.49359	0.50641	0.50641	0.50641
4s1p	14	210	0.31905	0.47142	0.49048	0.49524	0.49524
5s1p	16	272	0.25368	0.41176	0.44853	0.45588	0.45956
5s2p	22	506	0.20553	0.31423	0.37154	0.43874	0.40119
6s2p	24	600	0.17167	0.30167	0.37833	0.39500	0.40500
7s2p	26	702	0.15812	0.27778	0.35755	0.37749	0.39316
8s2p	28	812	0.14039	0.25000	0.32512	0.34975	0.37315
8s3p	34	1190	0.13109	0.21681	0.29916	0.34286	0.36134
9s3p	36	1332	0.11712	0.20195	0.28003	0.32508	0.34610
10s3p	38	1482	0.10594	0.18893	0.26316	0.30972	0.33941
11s3p	40	1640	0.10305	0.17500	0.24329	0.30000	0.32561
11s4p	46	2162	0.09343	0.16698	0.23127	0.28631	0.31915
12s4p	48	2352	0.08631	0.15221	0.21088	0.26531	0.29847
13s4p	50	2550	0.07882	0.13922	0.19333	0.24588	0.27490
14s4p	52	2756	0.07438	0.13171	0.18541	0.23403	0.27104
14s5p	58	3422	0.06517	0.11894	0.16774	0.21566	0.24839
15s5p	60	3660	0.06421	0.11339	0.15984	0.20628	0.24809
16s5p	62	3906	0.06042	0.10701	0.15182	0.19636	0.23374
17s5p	64	4160	0.05433	0.10096	0.14663	0.18510	0.22524
17s6p	70	4970	0.05131	0.09598	0.13461	0.17445	0.21288
18s6p	72	5256	0.04909	0.09170	0.13033	0.16591	0.20358

[a] includes orbital products $(\phi_i \phi_j)$ and derivatives $(\frac{d}{dR}\phi_i \phi_j)$

Table 5 Least squares optimal values of α, β, and γ for the function $r = \alpha\tanh(\beta M^{\gamma})$ at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{15} for C_2 two-electron integrals.

tolerance	α	β	γ
10^{-03}	186	0.011401	1.063459
10^{-06}	400	0.007137	1.173166
10^{-09}	528	0.003003	1.454537
10^{-12}	726	0.001181	1.679749
10^{-15}	1012	0.000665	1.761226

Table 6 Least squares optimal values of α, β, and γ for the function $r = \alpha \tanh(\beta M^{\gamma})$ at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{15} for C_2 two-electron integrals and derivatives

tolerance	α	β	γ
10^{-03}	326	0.013045	1.027928
10^{-06}	605	0.007877	1.143445
10^{-09}	772	0.003882	1.360329
10^{-12}	977	0.001807	1.551929
10^{-15}	1324	0.001100	1.616605

Table 7 Fraction of rank at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for C_2 two-electron integrals and integrals plus derivatives for the Dunning and 6-311g basis sets.

basis set	# basis function	full rank	frac.of rank at 10**-3	frac.of rank at 10**-6	frac.of rank at 10**-9	frac.of rank at 10**-12	frac.of rank at 10**-15
Dunning integrals	28	406	0.15517	0.34236	0.50985	0.56897	0.58128
6-311g integrals	26	351	0.19088	0.36752	0.45014	0.47009	0.48718
Dunning integrals + derivatives	28	812	0.14039	0.25123	0.33867	0.36823	0.37438
6-311g integrals + derivatives	26	702	0.16524	0.25783	0.31624	0.31197	0.32051

Table 8 Fraction of rank at cutoff tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15} for benzene two-electron integrals and integrals plus derivatives with an STO-3G basis.

type of calc.	# basis functions	full rank	frac.of rank at 10**-3	frac.of rank at 10**-6	frac.of rank at 10**-9	frac.of rank at 10**-12	frac.of rank at 10**-15
integrals	36	666	0.14414	0.31081	0.46547	0.58859	0.63814
integrals + derivatives	36	1332	0.15165	0.31081	0.46547	0.58859	0.63814

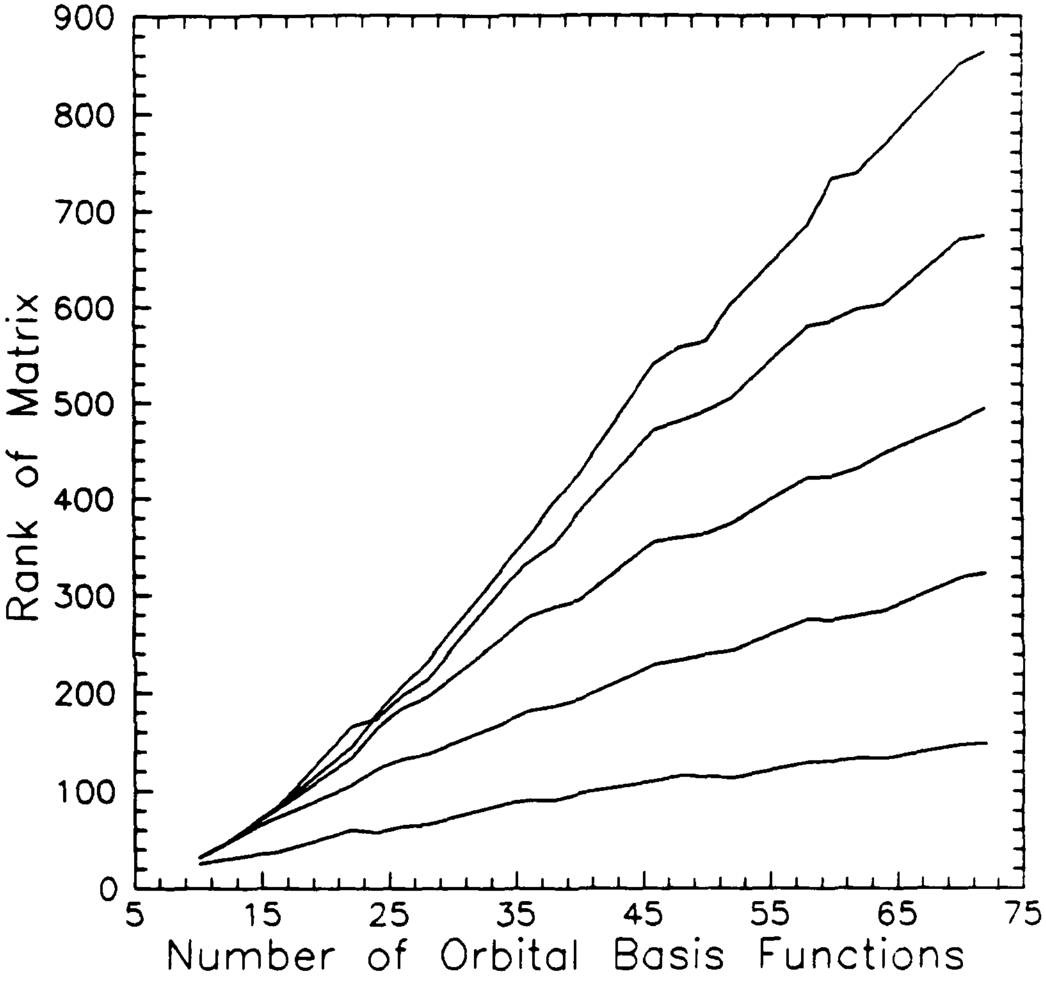

Figure 1. **Rank reduction for diatomic carbon two-electron integrals with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.**

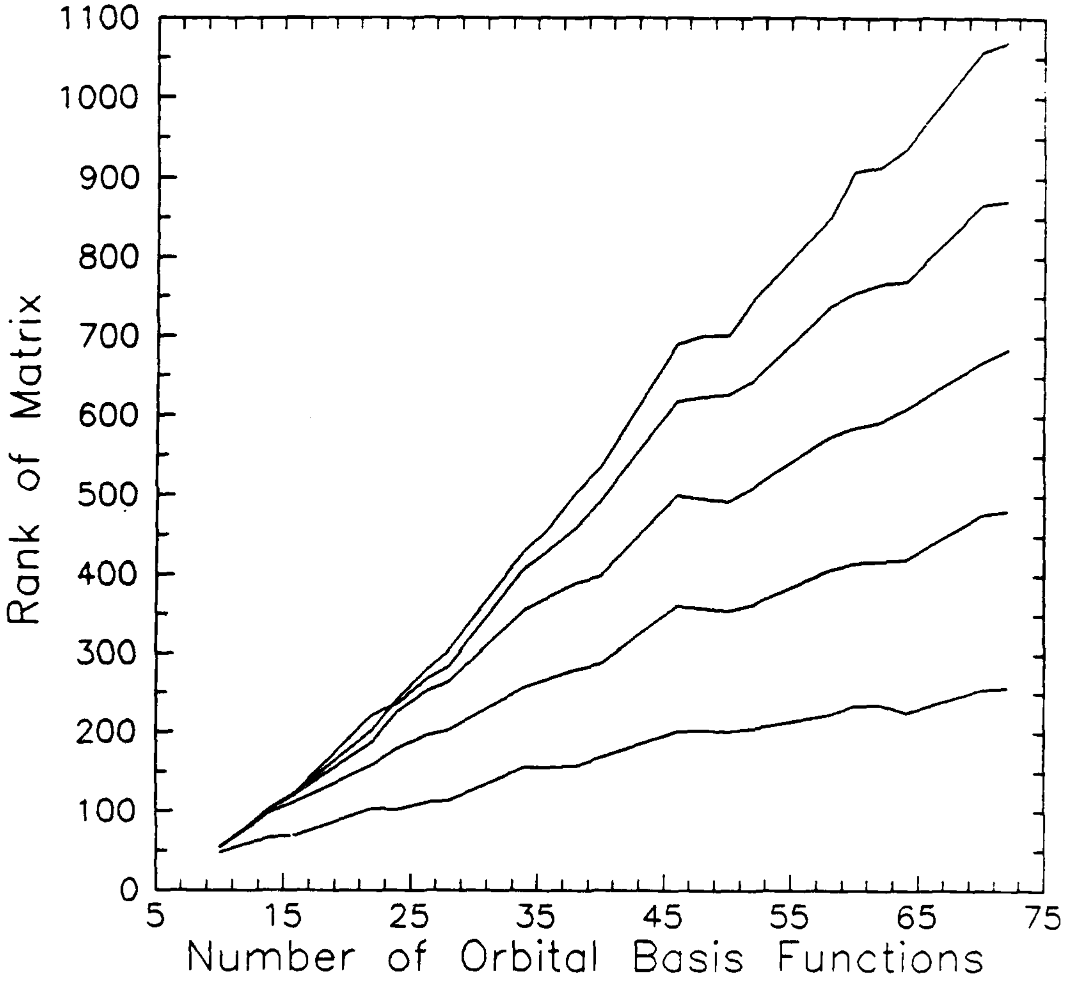

Figure 2. **Rank reduction for diatomic carbon two-electron integrals and derivatives with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.**

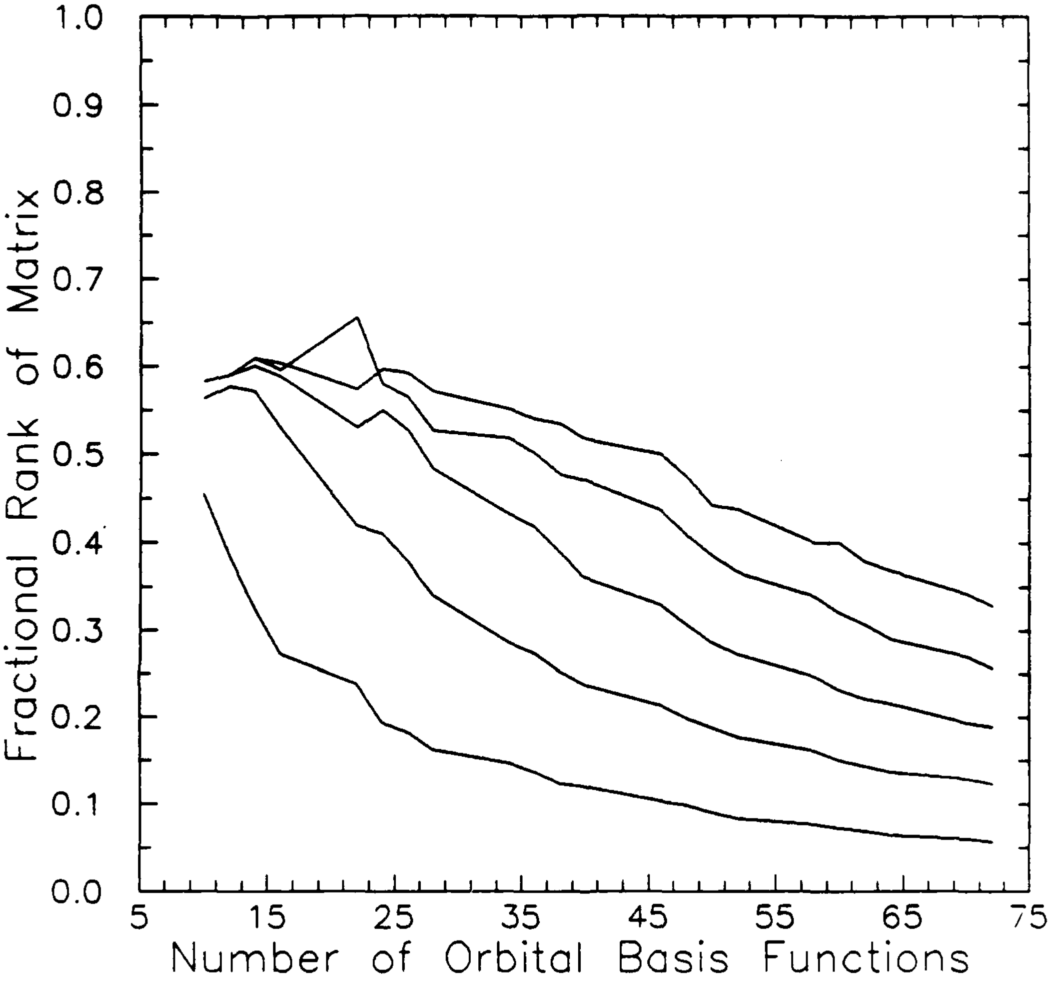

Figure 3. **Fractional rank r/M for diatomic carbon two-electron integrals with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.**

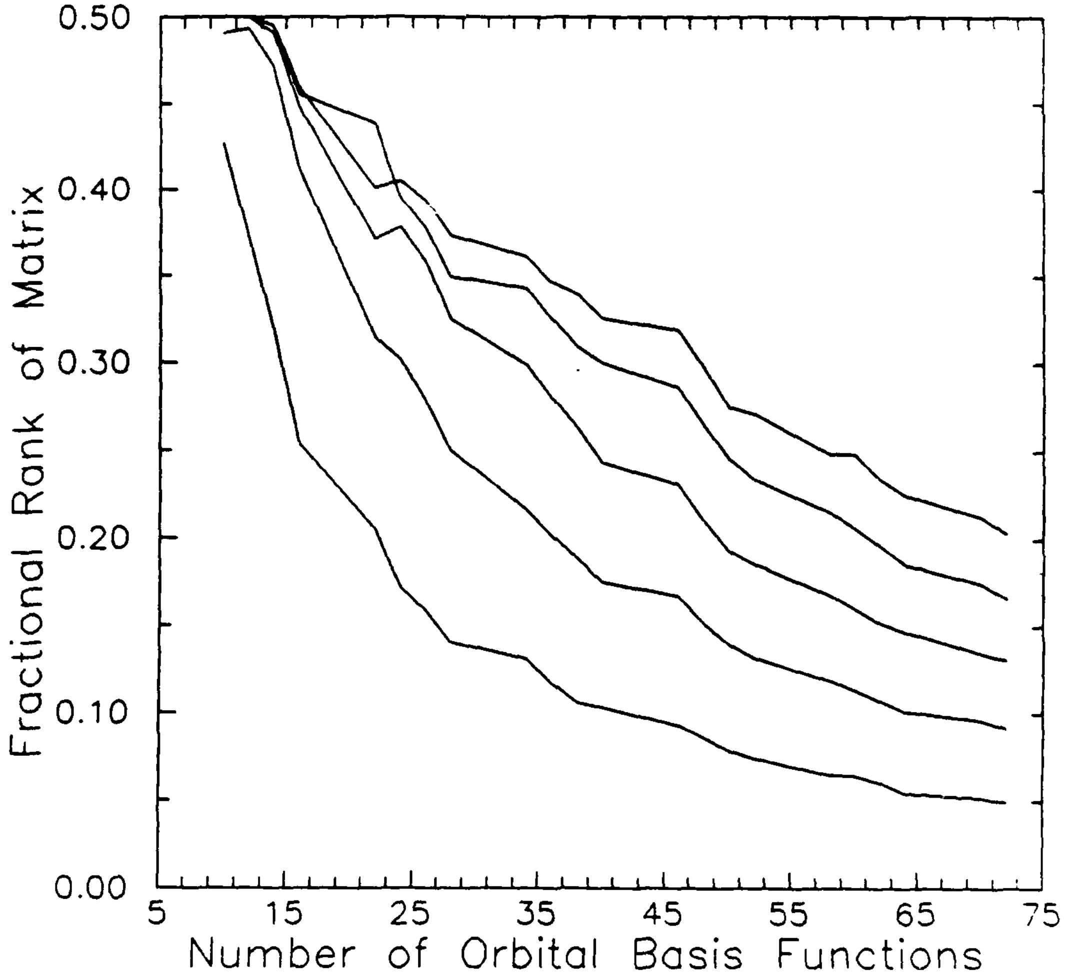

Figure 4. **Fractional rank r/M for diatomic carbon two-electron integrals and derivatives with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.**

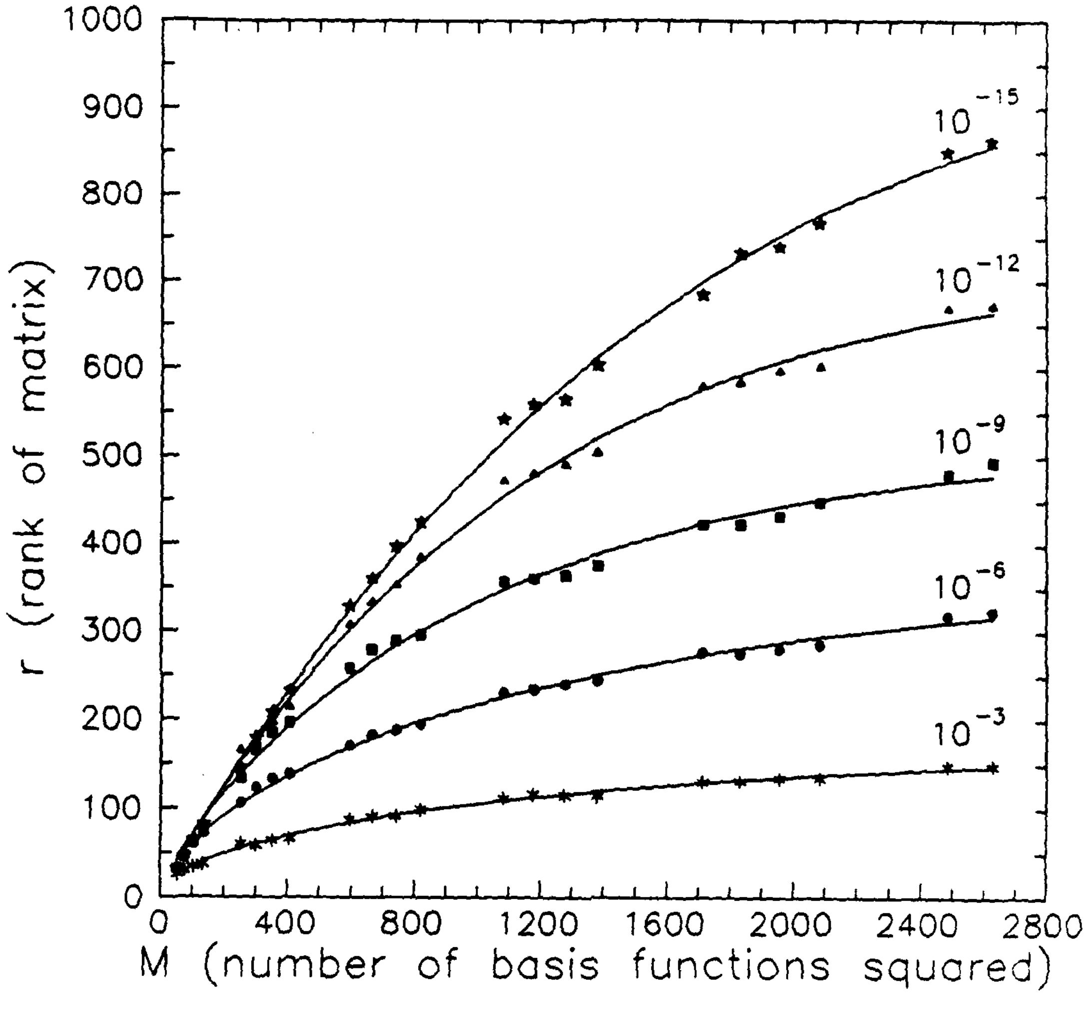

Figure 5. Least squares fit to actual data for diatomic carbon two-electron integrals with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.

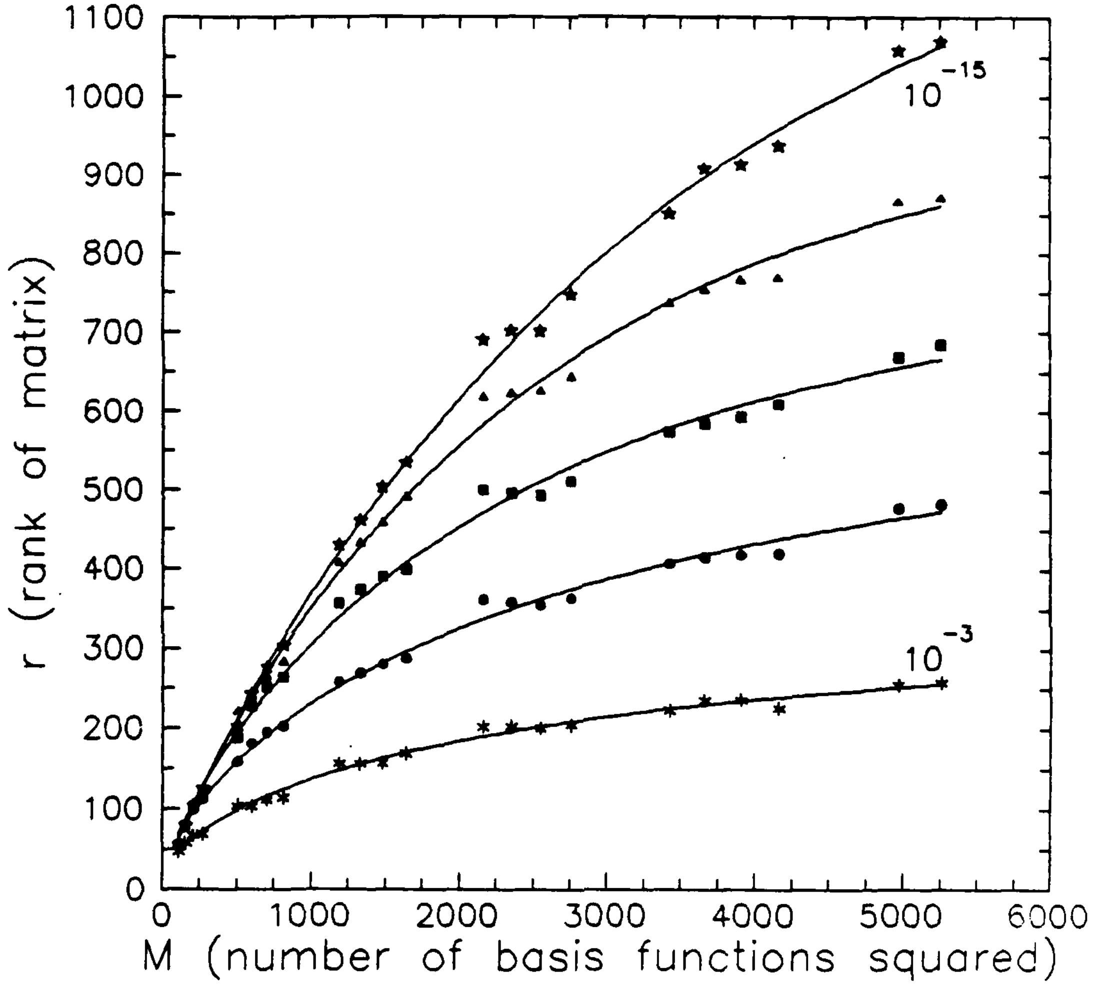

Figure 6. Leasts squares fit to actual data for diatomic carbon two-electron integrals and derivatives for even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.

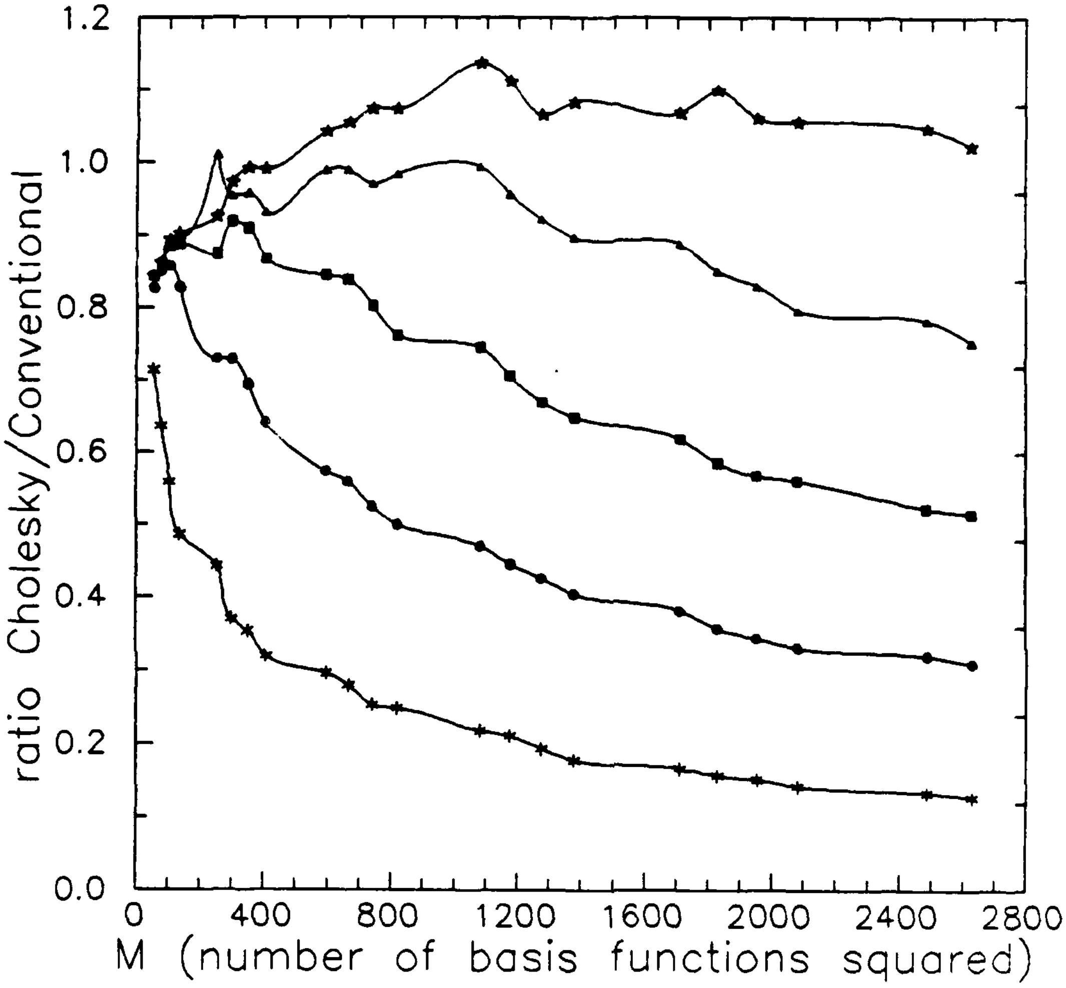

Figure 7. Ratio of CPU time weighted arithemetic operactions[a] for Cholesky algorithm to conventional methods for diatomic carbon two-electron integrals with even-tempered basis sets at tolerances 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.

[a] Integral evaluation time (503 μsec) and floating point multiplication (0.540 μsec) are included in these timings (see text).

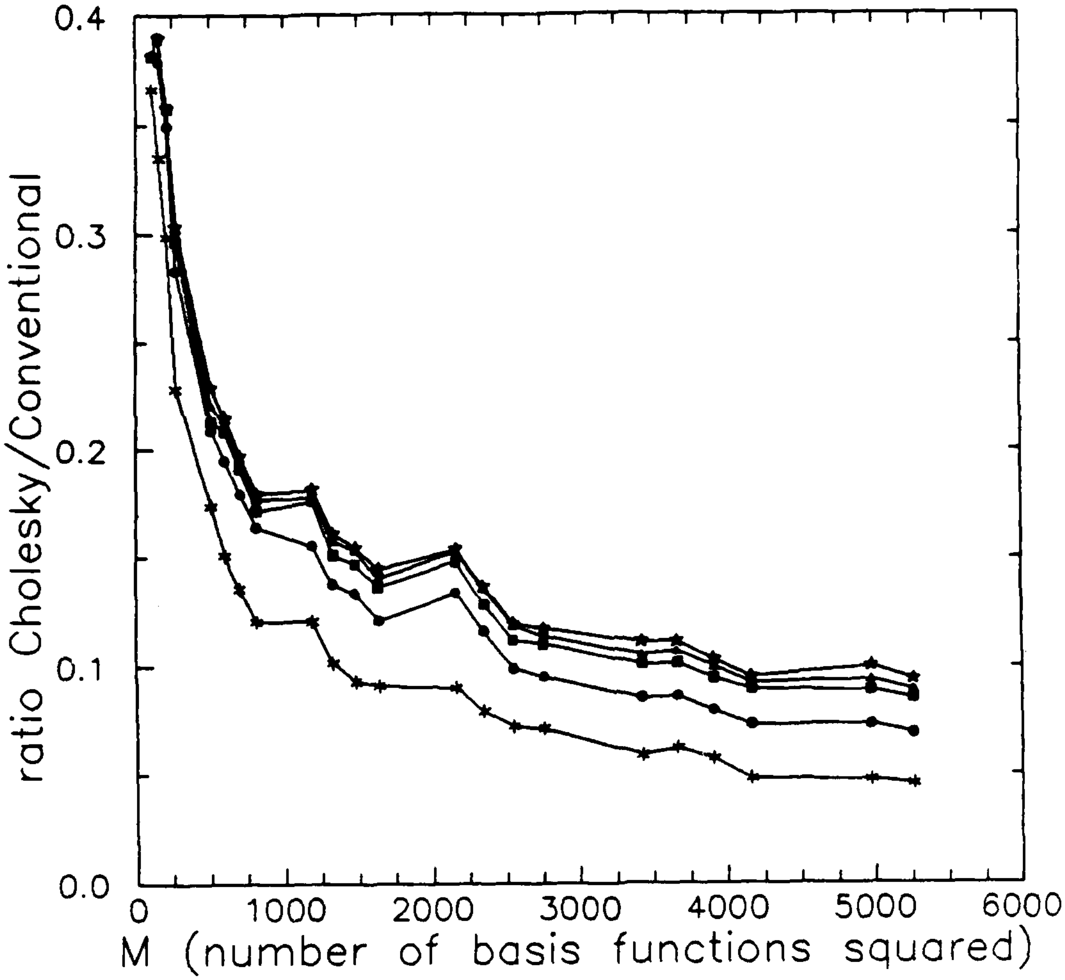

Figure 8. **Ratio of CPU time weighted arithemetic operactions[a] for Cholesky algorithm to conventional methods for diatomic carbon two-electron integrals and derivatives with even-tempered basis sets at tolerances of 10^{-3}, 10^{-6}, 10^{-9}, 10^{-12}, and 10^{-15}.**