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Universal Systematic Sequence of Even-Tempered Gaussian Primitive Functions in Electronic Correlation Studies

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The possibility of developing a universal systematic sequence of even-tempered Gaussian primitive functions for atomic and molecular electronic structure studies is examined. The radial beryllium-like ions are used to demonstrate this approach both within the Hartree–Fock model and by including correlation effects. Correlation energies are computed using the diagrammatic many-body perturbation theory. The Hartree extrapolation procedure is used to obtain empirical upper bounds to the basis set limit and the procedure of Schmidt and Ruedenberg is employed to obtain empirical lower bounds for the basis set limit. The convergence properties of the calculations with respect to the size of the basis set are examined.

Key words: Basis set – Even-tempered basis set – Universal basis set – Correlation energy – Many-body perturbation theory.

1. Introduction

In most applications of quantum mechanics to atoms and molecules the N-electron wave function is expressed in terms of the Nth rank direct product space generated by a finite dimensional single particle space. The accuracy of atomic and molecular calculations is ultimately determined by the degree of completeness of the basis set used to parameterise the single particle functions employed in the construction of the N-electron wave function. No amount of configuration mixing will compensate for a poor choice of basis functions. The result obtained by performing a full configuration interaction calculation, within a given Nth rank direct product space, will only approach the complete configuration interaction result as the basis set approaches completeness.

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In this paper, two recent developments in the construction of basis sets for accurate atomic and molecular calculations are combined. The concept of a universal basis set [1–5] is employed in conjunction with a systematic sequence of basis sets [6, 7] to examine convergence of calculations with respect to basis set size.

Accurate calculations necessitate the use of moderately large basis sets. Large basis sets have, of course, a considerable degree of flexibility and are, therefore, transferable from system to system with little loss in accuracy. These considerations have led to the concept of a universal basis set; a single basis set which can be used for any atom without regard to its nuclear charge or molecular environment. For example, recently reported calculations on the nitrogen, carbon monoxide and boron fluoride molecules using a universal basis set of even-tempered Slater exponential functions have led to some of the most accurate *ab initio* correlation energies for these systems reported to date [5]. The same list of integrals over the Slater basis functions was used in calculations on each of these molecules at a given nuclear geometry.

Ruedenberg and coworkers [6, 7] have recently devised schemes for systematically extending basis sets of the even-tempered type. They have applied their scheme to a considerable number of atomic systems using sets of Gaussian primitives within the Hartree–Fock molecular orbital model. In the work of Ruedenberg and his coworkers a different sequence of basis sets is used for different atoms. The present author has also examined the application of systematic schemes for extending basis sets in atomic calculations which include electron correlation effects [8]. Empirical procedures have been devised to provide empirical upper and lower bounds for the basis set limit.

In using the large basis sets which are required in accurate calculations, problems can arise from computational linear dependence and numerical instability. The degree of linear dependence can be reduced by using an even-tempered basis set [9–14]. The primitive basis set cannot become linearly dependent if the even-tempered concept is employed.

The use of a universal systematic sequence of even-tempered basis sets in electron correlation studies is proposed and discussed in this paper. In this work, the same sequence of basis sets will be used for different atoms. Illustrative calculations for radial beryllium-like ions are described, both within the Hartree–Fock model and including electron correlation. Theoretical and computational aspects of the present work are described in Sect. 2. The results are presented in Sect. 3 and discussed in Sect. 4.

2. Theoretical and Computational Aspects

The orbital exponents of an even-tempered basis set are defined by the geometric series

$$\zeta_k = \alpha\beta^k, \qquad k = 1, 2, \ldots, n$$

This ensures that the metric matrix has the structure

$$S_{i,j} = S_{i+1,j+1} \qquad \forall_{i,j}$$

Ruedenberg et al. [9] suggest that such a "basis 'covers' the Hilbert space evenly, i.e. that no part of the Hilbert space intercepted by the basis set is covered better than any other part, except near the boundary of this finite subspace".

Since $\alpha \to 0$, $\beta \to 1$ and $\beta^n \to \infty$ as the size of the basis set, n, tends to infinity, the empirical forms

$$\ln \ln \beta = b \ln n + b'$$

and

$$\ln \alpha = a \ln (\beta - 1) + a'$$

have been suggested [7] as a systematic scheme for extending even-tempered basis sets. This scheme has been shown to be useful within the Hartree–Fock model [6, 7] and in calculations [8] which take account of electron correlation effects. In this paper, we take the values of a, a', b and b' given by Schmidt and Ruedenberg [7] for the beryllium atom; namely

$$a = +0.3274$$

$$a' = -4.1916$$

$$b = -0.5230$$

$$b' = +1.3299$$

and use these basis sets to perform calculations on the series of beryllium-like ions Li^-, Be, B^+, C^{2+}, N^{3+}, O^{4+}, F^{5+} and Ne^{6+}.

The calculations reported in this paper were performed on the IBM 370/165 computer at the Science Research Council's Daresbury Laboratory.

Integrals over Gaussian functions, self-consistent-field calculations and orbital transformation phases of the computations were performed by means of the programs described in reference [15]. Basis sets comprising n s functions (denoted by $[ns]$) where $n = 6, 8, 10, 12, 14, 16, 18, 20$ were used in the calculations. The same integrals over the Gaussian basis functions were used in all of the calculations reported in this paper for a given n.

The electron correlation energies were calculated by means of the diagrammatic many-body perturbation theory [16]. The perturbation expansion with respect to the Hartree–Fock model zero-order hamiltonian, that is the expansion of Møller and Plesset [17, 18], was taken to third order and the [2/1] Padé approximants to the correlation energy constructed [19]. The [2/1] Padé approximants have special invariance properties which makes their use attractive [20, 21]. Computer programs for performing these correlation energy calculations have been described in detail previously [22–24].

3. Results

The results of the matrix Hartree–Fock calculations on each of the beryllium-like species considered in this work are presented in Table 1. The correlation energy corrections obtained by taking the many-body perturbation series to third-order and constructing [2/1] Padé approximants are given in Table 2. In Fig. 1, the quantity ln $(E[n''s]-E[n's])$ is plotted as a function of the basis set size, n, for all of the results presented in Table 1. The calculated correlation energies are plotted in Fig. 2 as a function of the basis set size.

4. Discussion

All of the energy values given in Table 1 decrease monotonically with increasing size of the basis set. The matrix Hartree–Fock energies for the Be atom and the positive ions appear to converge fairly uniformly for basis sets larger than [12*s*]. For the Li^- ion, the only negatively charged species considered in this work, the rate of convergence with respect to the basis set size is much slower than for the Be atom and the positively charged beryllium-like species. The valence electrons in the negative ion are much less tightly bound than the corresponding electrons in the neutral and positively charged ions and the energy is therefore much more sensitive to the degree of completeness of the basis set. This point is demonstrated further in Fig. 1. In this Figure it can be seen that the energies of the neutral and positively charged species converge at much the same rate. This demonstrates that

Table 1. Self-consistent-field energies for radial beryllium-like ions using the systematic sequence of even-tempered basis sets given by Schmidt and Ruedenberg [7] for the beryllium atom in all calculations*

Set	Li^-	Be	B^+	C^{2+}
[6*s*]	−7.251483	−14.534897	−24.140509	−36.230813
[8*s*]	−7.340599	−14.566442	−24.222327	−36.370037
[10*s*]	−7.375098	−14.571727	−24.234213	−36.401311
[12*s*]	−7.392530	−14.572705	−24.236807	−36.406797
[14*s*]	−7.402651	−14.572951	−24.237357	−36.408060
[16*s*]	−7.409097	−14.573002	−24.237519	−36.408360
[18*s*]	−7.413453	−14.573017	−24.237559	−36.408456
[20*s*]	−7.416529	−14.573021	−24.237570	−36.408484
	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
[6*s*]	−50.707427	−67.556801	−86.799882	−108.369858
[8*s*]	−51.013464	−68.141040	−87.721091	−109.752689
[10*s*]	−51.068088	−68.229240	−87.888102	−110.039519
[12*s*]	−51.078704	−68.251575	−87.923368	−110.092447
[14*s*]	−51.081409	−68.256090	−87.931103	−110.106434
[16*s*]	−51.082079	−68.257228	−87.933262	−110.109737
[18*s*]	−51.082241	−68.257567	−87.933821	−110.110602
[20*s*]	−51.082290	−68.257669	−87.933972	−110.110885

* All energies are in Hartree atomic units.

Table 2. Correlation energies for radial beryllium-like ions using the systematic sequence of even-tempered basis sets given by Schmidt and Ruedenberg [7] for the beryllium atom in all calculations*

Set	Li^-	Be	B^+	C^{2+}
[6*s*]	15.302	17.140	17.435	15.687
[8*s*]	16.444	18.089	17.250	17.238
[10*s*]	17.079	18.322	17.581	17.101
[12*s*]	17.469	18.384	17.622	17.207
[14*s*]	17.859	18.421	17.639	17.244
[16*s*]	18.113	18.434	17.655	17.251
[18*s*]	18.477	18.440	17.662	17.259
[20*s*]	18.725	18.444	17.666	17.264
	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
[6*s*]	16.653	17.193	16.192	15.055
[8*s*]	16.579	16.308	16.515	16.539
[10*s*]	16.900	16.786	16.541	16.408
[12*s*]	16.971	16.759	16.662	16.583
[14*s*]	16.980	16.820	16.688	16.579
[16*s*]	17.003	16.828	16.699	16.607
[18*s*]	17.009	16.848	16.710	16.612
[20*s*]	17.013	16.840	16.713	16.616

*All energies are in millihartree with signs reversed. The correlation energies given are [2/1] Padé approximants to the many-body perturbation expansion through third-order using a matrix Hartree–Fock zero-order operator.

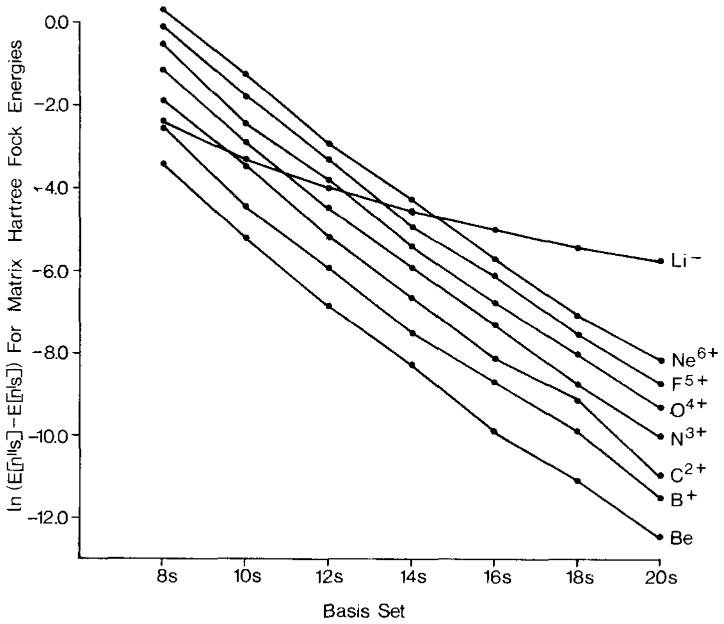

Fig. 1. Plot of ln $(E[n''s]-E[n's])$ against basis set size for the self-consistent-field energies

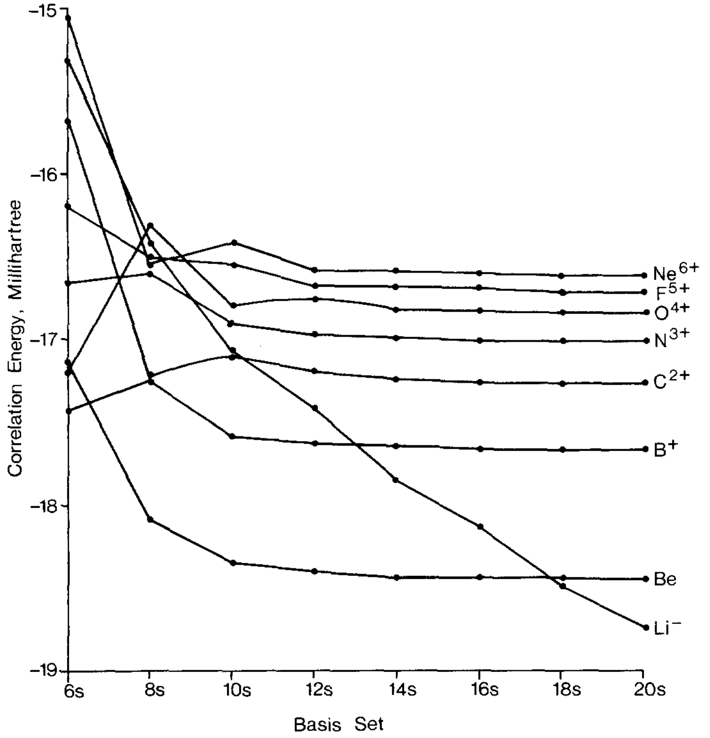

Fig. 2. Plot of the correlation energy, given by the [2/1] Padé approximant to the third-order energy, against basis set size

there is little dependence on the precise nature of the beryllium-like entity being studied while a series of basis sets specifically designed for the beryllium atom is being employed. For the Be atom the difference between the matrix Hartree–Fock energy calculated with the [18*s*] basis set and that calculated with the [20*s*] basis set is 0.004 mH, for B^+ this difference increases to 0.011 mH, for C^{2+} 0.028 mH, for N^{3+} 0.049 mH, for O^{4+} 0.102 mH, F^{5+} 0.151 mH and Ne^{6+} 0.283 mH. The degree of convergence, as measured by the difference between $E[20s]$ and $E[18s]$, deteriorates slightly as the nuclear charge is increased but nevertheless is still within 1 mH, which is usually regarded as "chemical accuracy". On the other hand, for the Li^- ion, the difference between $E[18s]$ and $E[20s]$ is approximately 3 mH.

In contrast to the matrix Hartree–Fock energies given in Table 1, the correlation energies given in Table 2 do not always decrease with an increase in the size of the basis set. These correlation energies are calculated perturbatively and do not, therefore, provide rigorous upper bounds to the energy. Convergence does, however, appear to be fairly uniform for basis sets larger than the [12*s*] set as is shown in Fig. 2. Again for the only negative ion studied, Li^-, there is a strong dependence on the degree of completeness of the basis set. Even for the largest basis sets considered in the present work, the results for the Li^- ion are still basis set dependent. For the Be atom and all of the positive ions the difference between $E[18s]$ and $E[20s]$ is less than 10 μH. For the Li^- ion this difference is ~250 μH.

Following the work of Schmidt and Ruedenberg [7], we have used the results presented in Tables 1 and 2 to derive empirical upper bounds and lower bounds to the total energies of each of the systems considered in this paper in the s basis set limit. The Hartree extrapolation [25, 26], which may be written as

$$E_\infty[n'''s]=(E[n'''s]E[n's]-E[n''s]^2)/(E[n'''s]-2E[n''s]+E[n's])$$

where n', n'', n''' are successive values of n, provides an empirical upper bound to the basis set limit [7]. However, it should be used with care and applied to a series of energy values to ensure that the energy is a reasonably smooth function of the basis set size. Hartree's extrapolation technique is based on the assumption that

$$(E[n''s]-E_\infty)=m(E[n's]-E_\infty)$$

where E_∞ is the true basis set limit. By considering three successive values of $E[ns]$, we can eliminate m and thus obtain an estimate of E_∞, which we denote by $E_\infty[ns]$. We can also find a value of m by considering three successive energy values and eliminating E_∞, giving

$$m=(E[n'''s]-E[n''s])/(E[n''s]-E[n's]).$$

The value of $m[ns]$ provides a useful indicator of the convergence properties of the energy values with increasing basis set size. If $|m|<1$ then the series of energy values is converging, whereas if $|m|>1$ it is diverging. If $m>0$ then the series of energy values behaves monotonically, while if $m<0$ then the series is oscillatory. Schmidt and Ruedenberg [7] have proposed that the expression

$$\hat{E}_\infty[ns]=E_\infty[ns]-(E[ns]-E_\infty[ns])$$

provides an empirical lower bound to the basis set limit. They demonstrated the use of this formula for a number of atoms within the Hartree–Fock model. The present author has investigated the use of this empirical procedure for calculations which include electron correlation effects [8]. The average energy [7]

$$E_{av}[ns]=\tfrac{1}{2}(E_\infty[ns]+\hat{E}_\infty[ns])$$

may be regarded as a "best" estimate of the basis set limit and the difference [7]

$$D[ns]=\tfrac{1}{2}(E_\infty[ns]-\hat{E}_\infty[ns])$$

as an estimate of the accuracy which may be given to this "best" value.

In Table 3, we give values of the empirical upper bound, $E_\infty[ns]$, the empirical lower bound, $\hat{E}_\infty[ns]$, the "best" energy, $E_{av}[ns]$, and $D[ns]$, the estimated accuracy, for the Hartree–Fock calculations described above. The corresponding quantities for energies which include correlation effects given in Table 2 are displayed in Table 4. For all of the calculations performed in this work, it can be seen from Tables 3 and 4 that $D[18s]>D[20s]$ indicating that convergence with respect to basis set size is being obtained. However, the values of $D[ns]$ obtained for Li^- are considerably larger than those obtained for the neutral and positively

Table 3. Empirical upper and lower bounds to the Hartree–Fock energy, "best" Hartree–Fock energy values and estimated accuracy*

	System	$E_\infty[ns]$	$\hat{E}_\infty[ns]$	$E_{av}[ns]$	$D[ns]$
Li^-	[18*s*]	−7.42254	−7.43162	−7.42708	4.54
	[20*s*]	−7.42391	−7.43129	−7.42760	3.69
Be	[18*s*]	−14.57302	−14.57303	−14.57303	0.00
	[20*s*]	−14.57302	−14,57303	−14.57302	0.00
B^+	[18*s*]	−24.23757	−24.23759	−24.23758	0.01
	[20*s*]	−24.23757	−24.23759	−24.23758	0.00
C^{2+}	[18*s*]	−36.40850	−36.40855	−36.40852	0.02
	[20*s*]	−36.40850	−36.40851	−36.40850	0.01
N^{3+}	[18*s*]	−51.08229	−51.08234	−51.08232	0.03
	[20*s*]	−51.08231	−51.08233	−51.08232	0.01
O^{4+}	[18*s*]	−68.25771	−68.25786	−68.25778	0.07
	[20*s*]	−68.25771	−68.25776	−68.25774	0.02
F^{5+}	[18*s*]	−87.93402	−87.93421	−87.83411	0.10
	[20*s*]	−87.93403	−87.93408	−87.93406	0.03
Ne^{6+}	[18*s*]	−110.11110	−110.11122	−110.11106	0.15
	[20*s*]	−110.11102	−110.11116	−111.11109	0.07

*All energies are in Hartree atomic units; $D[ns]$ is in millihartree.

charged species. Similarly, for all of the energies $E_{av}[ns]$ given in Tables 3 and 4 there is a change of less than 80 μH between the results obtained using the [18*s*] and the [20*s*] basis set for the beryllium atom and the positive ions. For the Li^- ion this difference is less than 1 mH.

Table 4. Empirical upper and lower bounds to the [2/1] Padé approximant to the total energy; "best" total energy values and estimated accuracy*

	System	$E_\infty[ns]$	$\hat{E}_\infty[ns]$	$E_{av}[ns]$	$D[ns]$
Li^-	[18*s*]	−7.44202	−7.45211	−7.44707	5.05
	[20*s*]	−7.44362	−7.45198	−7.44780	4.18
Be	[18*s*]	−14.59147	−14.59148	−14.59147	0.01
	[20*s*]	−14.59147	−14.59147	−14.59147	0.00
B^+	[18*s*]	−24.25524	−24.25525	−24.25525	0.01
	[20*s*]	−24.25524	−24.25525	−24.25525	0.01
C^{2+}	[18*s*]	−36.42577	−36.42582	−36.42580	0.03
	[20*s*]	−36.42576	−36.42578	−36.42577	0.01
N^{3+}	[18*s*]	−51.09931	−51.09936	−51.09933	0.03
	[20*s*]	−51.09933	−51.09935	−51.09934	0.01
O^{4+}	[18*s*]	−68.27455	−68.27470	−68.27463	0.08
	[20*s*]	−68.27456	−68.27460	−68.27458	0.02
F^{5+}	[18*s*]	−87.90574	−87.95095	−87.95084	0.10
	[20*s*]	−87.95074	−87.95080	−87.95077	0.03
Ne^{6+}	[18*s*]	−110.12752	−110.12783	−110.12768	0.15
	[20*s*]	−110.12764	−110.12778	−110.12771	0.07

*All energies are in Hartree atomic units; $D[ns]$ is in millihartree.

Table 5. Values of $m[ns]$ for $n = 18$ and 20

System	Hartree–Fock Energy		[2/1] Padé Approximant	
	$m[18s]$	$m[20s]$	$m[18s]$	$m[20s]$
Li^-	+0.68	+0.71	+0.68	+0.72
Be	+0.30	+0.33	+0.33	+0.38
B^+	+0.25	+0.28	+0.26	+0.33
C^{2+}	+0.32	+0.29	+0.34	+0.32
N^{3+}	+0.24	+0.30	+0.24	+0.31
O^{4+}	+0.30	+0.30	+0.30	+0.31
F^{5+}	+0.26	+0.27	+0.27	+0.27
Ne^{6+}	+0.26	+0.33	+0.26	+0.33

In Table 5 values of $m[18s]$ and $m[20s]$ are given for all of the systems examined in this work. All of the values of m are greater than zero indicating monotonic behaviour. Furthermore, for all of the systems studied $|m| < 1$, indicating that the energies are converging as the basis set is increased in size.

The calculations reported in this work have demonstrated that the concept of a universal sequence of basis sets will prove useful in systematic atomic and molecular calculations both within the Hartree–Fock model and in calculations which take account of electron correlation. The systematic sequence of even-tempered Gaussian primitive basis functions given by Schmidt and Ruedenberg [7] for the beryllium atom has been used in a study of eight beryllium-like ions. It has been found to be useful in calculations on neutral and positive charged species. For Li^- the convergence with respect to basis set size is not so good as for the other systems considered in this work because of the more diffuse nature of the orbitals involved.

References

1. Silver, D. M., Wilson, S., Nieuwpoort, W. C.: Intern. J. Quantum Chem. **14**, 635 (1978)
2. Silver, D. M., Nieuwpoort, W. C.: Chem. Phys. Letters **57**, 421 (1978)
3. Silver, D. M., Wilson, S.: J. Chem. Phys. **69**, 3787 (1978)
4. Wilson, S., Silver, D. M.: Chem. Phys. Letters **63**, 367 (1979)
5. Wilson, S., Silver, D. M.: J. Chem. Phys. **72**, 2159 (1980)
6. Feller, D. F., Ruedenberg, K.: Theoret. chim. Acta. (Berl.) **52**, 231 (1979)
7. Schmidt, M. W., Ruedenberg, K.: J. Chem. Phys. **71**, 3951 (1979).
8. Wilson S.: Theoret. chim. Acta. (Berl.) (1980) (in press)
9. Ruedenberg, K., Raffenetti, R. C., Bardo, R. D. in: Energy structure and reactivity. Proceedings of the 1972 Boulder Conference on Theoretical Chemistry, New York: Wiley 1973 see also: Reeves, C. M.: J. Chem. Phys. **39**, 1 (1963) Reeves, C. M., Harrison, M.: J. Chem. Phys. **39**, 11 (1963)
10. Raffenetti, R. C.: J. Chem. Phys. **59**, 5936 (1973)
11. Bardo, R. D., Ruedenberg, K.: J. Chem. Phys. **59**, 5956, 5966 (1973)
12. Raffenetti, R. C., Ruedenberg, K.: J. Chem. Phys. **59**, 5978 (1973)
13. Bardo, R. D., Ruedenberg, K.: J. Chem. Phys. **60**, 918 (1974)
14. Raffenetti, R. C.: J. Chem. Phys. **58**, 4452 (1973)
15. Guest, M. F., Saunders, V. R.: ATMOL3 User Manuals, Rutherford Laboratory, Science Research Council. (1976)

16. Wilson, S., Silver, D. M.: Phys. Rev. **A14**, 1949 (1976)
17. Møller, C., Plesset, M. S.: Phys. Rev. **46**, 618 (1934)
18. Pople, J. A., Binkley, J. S., Seeger, R.: Intern J. Quantum Chem. **10**, 1 (1976)
19. Wilson, S.: J. Phys. B: Atom. Molec. Phys. **12**, 1649 (1979)
20. Wilson, S., Silver, D. M., Farrell, R. A.: Proc. Roy. Soc. (London) **A356**, 363 (1977)
21. Amos, A. T.: Intern. J. Quantum Chem. **6**, 125 (1972)
22. Silver, D. M.: Comput. Phys. Commun. **14**, 71 (1978)
23. Silver, D. M.: Comput. Phys. Commun. **14**, 81 (1978)
24. Wilson, S.: Comput. Phys. Commun. **14**, 91 (1978)
25. Hartree, D. R.: Proc. Cambridge Philos. Soc. **45**, 230 (1948)
26. Roothaan, C. C. J., Bagus, P. S.: Methods in Comput. Phys. **2**, 47 (1963)

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