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Contracted well-tempered Gaussian basis sets in SCF calculations on the ground and excited electronic states of neutral and ionized diatomic molecules containing first-row atoms

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Summary. Calculations were done on ground and excited states of C_2, C_2^+, C_2^-, N_2, N_2^+, O_2, O_2^+, O_2^-, CO, CO^+, CO^{2+}, and CO^- using contracted well-tempered basis sets. The (14*s*10*p*) basis sets were augmented with three *d*, one or two *f*, and one *g* functions. Total energies, orbital energies, and spectroscopic constants were compared with the best available computational data.

Key words: Gaussian basis sets – SCF calculations – Diatomic molecules – Excited electronic states

Introduction

Recently, we have prepared a new collection of accurate Gaussian basis sets [1]. The new sets, called well-tempered [2], are flexible enough to give the atomic total energies which, for the first row atoms, differ from the Hartree–Fock values by less than 0.2 mE_h. In the contracted form and augmented with a set of three *d* functions, these basis sets were used in SCF calculations on the ground states of several diatomic molecules containing atoms from the first row of the periodic table (Li–Ne) [3] giving results fairly close to the available Hartree–Fock data. The remaining discrepancies were atrributed to the lack of *f* functions in the basis sets.

The well-tempered basis sets are equipped not only with large-exponent Gaussians (required for near-Hartree–Fock atomic total energies) but also with diffuse functions, which bring about acceptable values of atomic excitation energies without the need for augmenting the basis sets [4]. In molecular calculations, the well-tempered basis sets should be good candidates for "off the shelf" basis sets to be used in studies on both ground and excited states of neutral molecules and their positive and negative ions.

Fifteen years ago, Cade and Wahl [5] published a collection of results for homonuclear diatomic molecules composed of the first-row atoms. The wavefunctions for various electronic states were expanded in terms of a large set of Slater-type functions (STF) whose exponents were optimized in the molecular calculations for the ground electronic states near equilibrium internuclear distances. These wavefunctions were alleged to achieve true Hartree–Fock accuracy. The same basis sets, without reoptimization of exponents, were then used to obtain the wavefunctions for excited states of the neutral molecules and for the ground states of positively and negatively charged molecular ions. Due to the lack of exponent reoptimization, the values of the total energy for those systems were believed to be within 5 mE_h of the Hartree–Fock values.

In their calculations on heteronuclear diatomic molecules, Cade and Huo [6] had to restrict the size of the basis sets due to the computer memory limitations. They estimated that the basis sets used might give total energies as much as 5 to 10 mE_h from the Hartree–Fock limit.

Optimization of exponential parameters of STF basis sets in molecular calculations, performed by Cade and Wahl [5] and Cade and Huo [6], was possible due to a small number of individual Slater-type functions which had to be used for an accurate expansion of wavefunctions. In the case of Gaussian-type functions (GTF), an accurate basis set requires so many primitive GTFs that their optimization in molecular calculations is out of the question. We can only hope that it will be the large number of primitive GTFs, with their exponents optimized in atomic calculations, which will provide the Gaussian basis sets with the flexibility required in order to adequately span all regions of the SCF wavefunctions.

We decided to test the well-tempered basis sets for some of the systems studied by Cade and Wahl [5] and Cade and Huo [6]. Their results, due to a careful computational design, became benchmark results for ground and excited electronic states of diatomic molecules and their ions; they are the only results in which the same basis sets were systematically used in expanding the SCF wavefunctions for various electronic states at several internuclear distances. There are many excellent calculations for diatomics in which Gaussian basis sets were used; however, as none of them studied the basis sets deployed in the extensive manner of Cade and Wahl [5] and Cade and Huo [6], we did not use those results for comparison.

Today, numerical Hartree–Fock calculations for closed-shell ground states of diatomics can be performed [7]; however, the computational effort is still substantial, especially for open-shell systems [8]. On the other hand, matrix Hartree–Fock calculations in Gaussian basis sets are very easy to perform; and, as the present work shows, well-designed standard atomic basis sets are capable of providing excellent molecular results.

Table 1. Structure of the contracted basis set ($7s6p3d2f$)[a]

	($1s$	$2s$	$3s$	$4s$	$5s$	$6s$	$7s$)	($1p$	$2p$	$3p$	$4p$	$5p$	$6p$)	($1d$	$2d$	$3d$)	($1f$	$2f$)
ζ_1	a	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·
ζ_2	a	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·
ζ_3	a	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·
ζ_4	a	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·
ζ_5	a	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·	·
ζ_6	·	b	c	·	·	·	·	c	·	·	·	·	·	·	·	·	·	·
ζ_7	·	b	c	·	·	·	·	c	·	·	·	·	·	·	·	·	·	·
ζ_8	·	b	c	·	·	·	·	c	·	·	·	·	·	·	·	·	·	·
ζ_9	·	b	c	·	·	·	·	c	·	·	·	·	·	·	·	·	·	·
ζ_{10}	·	b	c	·	·	·	·	c	·	·	·	·	·	·	·	·	·	·
ζ_{11}	·	b	·	d	·	·	·	·	d	·	·	·	·	d	·	·	d	·
ζ_{12}	·	b	·	·	e	·	·	·	·	e	·	·	·	·	e	·	·	e
ζ_{13}	·	·	·	·	·	f	·	·	·	·	f	·	·	·	·	f	·	·
ζ_{14}	·	·	·	·	·	·	g	·	·	·	·	g	·	·	·	·	·	·
ζ_{15}	·	·	·	·	·	·	·	·	·	·	·	·	h	·	·	·	·	·

[a] The same letters in a column indicate that the primitive GTFs belong to the same contracted GTF; same letters in a row indicate that the (two) contracted (or uncontracted) GTFs belong to the same shell

Calculations

In the present work we studied the following systems (the valence electron configurations are given in parentheses):

$C_2[^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$, $C_2[^3\Sigma_g^-(1\pi_u^2 3\sigma_g^2)]$, $C_2[^1\Delta_g(1\pi_u^2 3\sigma_g^2)]$, $C_2[^1\Sigma_g^+(1\pi_u^2 3\sigma_g^2)]$, $C_2^+[^2\Pi_u(1\pi_u^3 3\sigma_g^0)]$, $C_2^-[^2\Pi_u(1\pi_u^3 3\sigma_g^2)]$, $C_2^-[^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$, $N_2[^1\Sigma_g^+(3\sigma_g^2 1\pi_u^4)]$, $N_2^+[^2\Sigma_g^+(3\sigma_g^1 1\pi_u^4)]$, $N_2^+[^2\Pi_u(3\sigma_g^2 1\pi_u^3)]$, $O_2[^3\Sigma_g^-(1\pi_u^4 1\pi_g^2)]$, $O_2[^1\Delta_g(1\pi_u^4 1\pi_g^2)]$, $O_2[^1\Sigma_g^+(1\pi_u^4 1\pi_g^2)]$, $O_2^+[^2\Pi_g(1\pi_u^4 1\pi_g^1)]$, $O_2^-[^2\Pi_g(1\pi_u^4 1\pi_g^3)]$, $CO[^1\Sigma^+(1\pi^4 5\sigma^2)]$, $CO^+[^2\Sigma^+(1\pi^4 5\sigma^1)]$, $CO^+[^2\Pi(1\pi^3 5\sigma^2)]$, and $CO^{2+}[^1\Sigma^+(1\pi^4 5\sigma^0)]$.

As the initial basis sets we used the contracted well-tempered sets designated (7*s*6*p*3*d*) which were fully described and compared with other contraction schemes in our previous work [3]. These basis sets were augmented by one *f*, two *f*, and two *f* plus one *g* functions, giving (7*s*6*p*3*d*1*f*), (7*s*6*p*3*d*2*f*), and (7*s*6*p*3*d*2*f*1*g*) basis sets, respectively. The structure of the contracted (7*s*6*p*3*d*2*f*) basis sets is given in Table 1. Table 2 collects the values of the exponential parameters in the well-tempered pool [1]. (Note that even though there are fifteen exponents in the pool, only fourteen of them are used to span the *s* space, cf. Table 1.) The expansion coefficients of the first two *s* contracted functions were taken from the expansion of the 1*s* atomic orbital in the ground state; the coefficients of the third *s* contracted function were taken from the 2*s* atomic orbital. (For the values of the coefficients see our compilation [1].) As shown in Table 1, the exponential parameters of the three *d* and of the two *f* functions in the (7*s*6*p*3*d*2*f*) basis set were taken from the exponent pool. The shell structure of the basis set will result in computer time savings if a properly coded integral program is available. The exponents of the single *f* and *g* functions were usually

Table 2. Values of the exponential parameters

	C	N	O
ζ_1	107248.11	168738.77	213517.27
ζ_2	17276.407	25391.428	35589.708
ζ_3	3779.8010	5642.9789	8047.2010
ζ_4	1000.7633	1486.2202	2116.2738
ζ_5	315.15754	459.83176	644.59271
ζ_6	114.98112	164.60066	226.37633
ζ_7	45.408915	64.118667	86.862138
ζ_8	18.705757	26.219014	35.220425
ζ_9	7.8380371	10.943127	14.627215
ζ_{10}	3.3261120	4.6320492	6.1719131
ζ_{11}	1.3699729	1.9109974	2.5476189
ζ_{12}	0.57908665	0.80546771	1.0715909
ζ_{13}	0.24205984	0.33620454	0.44624576
ζ_{14}	0.10107327	0.13996031	0.18548085
ζ_{15}	0.040473775	0.056451111	0.077157035

adjusted to approximately satisfy, in a single-function environment, the need for different values of the exponential parameters for σ and π spaces [5].

The molecular SCF calculations were done at a few points around the minimum of the SCF total energy curve; in this set we always included the internuclear distance for which details of the wavefunctions had been published [5, 6].

We used the SPDFG [9] integral package to evaluate the integrals over Cartesian Gaussians. The open-shell Hartree–Fock equations were solved using the formalism of Carbó and Riera [10]. All computations were performed on the Amdahl 5870 and FPS 164 processors at the University of Alberta.

Results

C_2, C_2^+, *and* C_2^-

In the calculations on various electronic states of C_2, C_2^+, and C_2^- we used the ($7s6p3d$), ($7s6p3d1f$), and ($7s6p3d2f$) basis sets. The exponential parameter of the single f function in the ($7s6p3d1f$) set was optimized in calculations on the ${}^1\Sigma_g^+$ state at $r = 2.3481$ a$_0$; the value adopted in all calculations was $\zeta_f = 1.0847$. The values of total and orbital energies are compared in Table 3 with the results of Cade and Wahl [5]. The values of the spectroscopic constants, obtained via polynomial fitting, are collected in Table 4.

Addition of a single, energy-optimized, f function to ($7s6p3d$) has the greatest effect (3 mE$_h$) for the system $C_2[{}^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$ for which the optimization was done. The single f function lowers the total energy most for the calculations performed at the same distance at which the exponential parameter was optimized (2.6 mE$_h$ for $C_2^+[{}^2\Pi_u(1\pi_u^3 3\sigma_g^0)]$, and 2.0 mE$_h$ for $C_2^-[{}^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$). The improvement of the total energy for the remaining systems, calculated at $r = 2.5876$ a$_0$, is smaller and varies from 1.2 mE$_h$ for $C_2^+[{}^2\Pi_u(1\pi_u^1 3\sigma_g^2)]$ to 0.7 mE$_h$ for $C_2[{}^3\Sigma_g^-(1\pi_u^2 3\sigma_g^2)]$. The basis set ($7s6p3d1f$) performs very well: except for $C_2[{}^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$ and $C_2[{}^3\Sigma_g^-(1\pi_u^2 3\sigma_g^2)]$ the total energies are lower than the values obtained by Cade and Wahl.

When the energy-optimized single f function is replaced by two f functions (with their exponential parameters taken from the well-tempered exponent pool, see Table 1), the values of total energy become slightly lower, usually by 0.1 mE$_h$. The ($7s6p3d2f$) total energies are better than the ones calculated by Cade and Wahl for all the systems, although the differences are smaller than 1 mE$_h$. The only exceptions are $C_2^+[{}^2\Pi_u(1\pi_u^1 3\sigma_g^2)]$, $C_2^-[{}^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$, and $C_2^-[{}^2\Pi_u(1\pi_u^3 3\sigma_g^2)]$ for which Cade and Wahl's STF basis set gives total energies 4.8, 8.5, and 17.5 mE$_h$ above our ($7s6p3d2f$) values, respectively.

The values of the spectroscopic constants change but slightly upon adding one or two f functions to the initial ($7s6p3d$) basis set. The equilibrium internuclear distances are shortened (by about 0.001 a$_0$) and the harmonic vibrational frequencies are increased. Replacing the single, optimized f function by two unoptimized f functions often lengthens the bond length insignificantly

Table 3. Total and orbital energies[a] and differences of total and orbital energies[b] for C_2, C_2^+, and C_2^- (in E_h)

Basis	E_T	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$
	$C_2[^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$			$r = 2.3481\ a_0$			
STF[c]	*−75.406200*	*−11.3598*	*−11.3575*	*−1.0613*	*−0.5172*	*−0.4579*	
($7s6p3d$)	0.002957	−0.0014	−0.0014	−0.0017	−0.0004	0.0004	
($7s6p3d1f$)	−0.000025	−0.0001	−0.0001	−0.0001	−0.0001	−0.0001	
($7s6p3d2f$)	−0.000054	−0.0001	−0.0001	−0.0001	0.0000	−0.0001	
	$C_2[^3\Sigma_g^-(1\pi_u^2 3\sigma_g^2)]$			$r = 2.5876\ a_0$			
STF[c]	*−75.515220*	*−11.3446*	*−11.3430*	*−1.0461*	*−0.5871*	*−0.4600*	*−0.4575*
($7s6p3d$)	0.000776	−0.0008	−0.0008	0.0015	0.0007	−0.0380	0.0006
($7s6p3d1f$)	0.000089	−0.0003	−0.0003	0.0023	0.0009	−0.0382	0.0011
($7s6p3d2f$)	−0.000014	−0.0002	−0.0003	0.0024	0.0008	−0.0382	0.0011
	$C_2[^1\Delta_g(1\pi_u^2 3\sigma_g^2)]$			$r = 2.5876\ a_0$			
STF[c]	*−75.476650*	*−11.3466*	*−11.3450*	*−1.0461*	*−0.5871*	*−0.4600*	*−0.4575*
($7s6p3d$)	0.000761	−0.0025	−0.0025	−0.0028	−0.0015	−0.0006	−0.0019
($7s6p3d1f$)	−0.000079	−0.0020	−0.0020	−0.0019	−0.0014	−0.0008	−0.0014
($7s6p3d2f$)	−0.000165	−0.0020	−0.0020	−0.0019	−0.0014	−0.0008	−0.0014
	$C_2[^1\Sigma_g^+(1\pi_u^2 3\sigma_g^2)]$			$r = 2.5876\ a_0$			
STF[c]	*−75.438500*	*−11.3487*	*−11.3471*	*−1.0487*	*−0.5880*	*−0.4227*	*−0.4586*
($7s6p3d$)	0.000462	−0.0045	−0.0045	−0.0048	−0.0031	−0.0015	−0.0036
($7s6p3d1f$)	−0.000555	−0.0039	−0.0039	−0.0038	−0.0029	−0.0019	−0.0030
($7s6p3d2f$)	−0.000629	−0.0039	−0.0039	−0.0038	−0.0029	−0.0019	−0.0030
	$C_2^+[^2\Pi_u(1\pi_u^3 3\sigma_g^0)]$			$r = 2.3481\ a_0$			
STF[c]	*−74.991960*	*−11.7742*	*−11.7720*	*−1.4518*	*−0.8631*	*−0.8493*	
($7s6p3d$)	0.001837	−0.0005	−0.0005	−0.0008	0.0006	0.0016	
($7s6p3d1f$)	−0.000776	0.0006	0.0006	0.0006	0.0008	0.0009	
($7s6p3d2f$)	−0.000873	0.0007	0.0007	0.0007	0.0008	0.0009	
	$C_2^+[^2\Pi_u(1\pi_u^1 3\sigma_g^2)]$			$r = 2.5876\ a_0$			
STF[c]	*−75.047030*	*−11.7628*	*−11.7612*	*−1.4493*	*−0.9405*	*−0.8679*	*−0.8139*
($7s6p3d$)	−0.003958	0.0080	0.0080	0.0079	0.0060	0.0053	0.0051
($7s6p3d1f$)	−0.004700	0.0084	0.0084	0.0086	0.0060	0.0050	0.0054
($7s6p3d2f$)	−0.004810	0.0085	0.0084	0.0087	0.0060	0.0048	0.0054
	$C_2^-[^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$			$r = 2.3481\ a_0$			
STF[c]	*−75.556700*	*−10.9660*	*−10.9633*	*−0.7191*	*−0.2159*	*−0.1189*	*−0.1974*
($7s6p3d$)	−0.006490	−0.0277	−0.0276	−0.0203	−0.0173	−0.0181	−0.0166
($7s6p3d1f$)	−0.008413	−0.0268	−0.0267	−0.0190	−0.0171	−0.0184	−0.0160
($7s6p3d2f$)	−0.008498	−0.0267	−0.0267	−0.0190	−0.0171	−0.0184	−0.0160
	$C_2^-[^2\Pi_u(1\pi_u^3 3\sigma_g^2)]$			$r = 2.5876\ a_0$			
STF[c]	*−75.563270*	*−10.9657*	*−10.9640*	*−0.6735*	*−0.2541*	*−0.1061*	*−0.1213*
($7s6p3d$)	−0.016660	−0.0503	−0.0504	−0.0436	−0.0331	−0.0321	−0.0345
($7s6p3d1f$)	−0.017474	−0.0498	−0.0499	−0.0428	−0.0330	−0.0322	−0.0339
($7s6p3d2f$)	−0.017541	−0.0499	−0.0500	−0.0428	−0.0330	−0.0322	−0.0339

[a] The STF reference values of total and orbital energies are printed in italic

[b] The differences of total and orbital energies are defined as E_T(basis) − E_T(STF reference)

[c] [5]

Table 4. Spectroscopic constants[a] of C_2, C_2^+, and C_2^-

Basis	M[b]	E_T	r_e	ω_e	$\omega_e x_e$	B_e	α_e	κ_e
		$C_2[^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$						
(7*s*6*p*3*d*)	4	−75.4032595	2.3417	1901.5	12.81	1.830	17.18	12.78
(7*s*6*p*3*d*1*f*)	4	−75.4061949	2.3411	1907.8	12.64	1.831	17.05	12.87
(7*s*6*p*3*d*2*f*)	4	−75.4062751	2.3410	1905.9	12.73	1.831	17.14	12.84
STF[c]	5	−75.40591	2.3407	1904.8	12.25	1.831	17.14	12.83
		$C_2[^3\Sigma_g^-(1\pi_u^2 3\sigma_g^2)]$						
(76*p*3*d*)	4	−75.5155317	2.5275	1675.6	8.229	1.571	13.24	9.925
(7*s*6*p*3*d*1*f*)	4	−75.5162586	2.5265	1679.6	8.368	1.572	13.23	9.973
(7*s*6*p*3*d*2*f*)	4	−75.5163606	2.5265	1679.4	8.390	1.572	13.24	9.971
		$C_2[^1\Delta_g(1\pi_u^2 3\sigma_g^2)]$						
(7*s*6*p*3*d*)	5	−75.4763261	2.5490	1637.1	8.223	1.544	12.91	9.474
(7*s*6*p*3*d*1*f*)	5	−75.4771952	2.5478	1641.4	8.318	1.546	12.92	9.525
(7*s*6*p*3*d*2*f*)	5	−75.4772797	2.5479	1640.9	8.375	1.546	12.95	9.519
		$C_2[^1\Sigma_g^+(1\pi_u^2 3\sigma_g^2)]$						
(7*s*6*p*3*d*)	5	−75.4381217	2.5705	1598.8	8.134	1.518	12.86	9.037
(7*s*6*p*3*d*1*f*)	5	−75.4391525	2.5692	1603.5	8.217	1.520	12.87	9.090
(7*s*6*p*3*d*2*f*)	5	−75.4392258	2.5693	1602.5	8.255	1.520	12.91	9.078
		$C_2^+[^2\Pi_u(1\pi_u^3 3\sigma_g^0)]$						
(7*s*6*p*3*d*)	5	−74.9964180	2.4850	1585.2	13.95	1.625	19.19	8.884
(7*s*6*p*3*d*1*f*)	5	−74.9989499	2.4836	1593.0	13.94	1.627	19.08	8.971
(7*s*6*p*3*d*2*f*)	5	−74.9990652	2.4840	1589.5	14.01	1.626	19.17	8.932
		$C_2^+[^2\Pi_u(1\pi_u^1 3\sigma_g^2)]$						
(7*s*6*p*3*d*)	4	−75.0626639	2.8207	1230.1	8.288	1.261	12.90	5.350
(7*s*6*p*3*d*1*f*)	4	−75.0632627	2.8189	1232.9	8.372	1.263	12.95	5.374
(7*s*6*p*3*d*2*f*)	4	−75.0633927	2.8192	1232.0	8.324	1.262	12.97	5.365
		$C_2^-[^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$						
(7*s*6*p*3*d*)	5	−75.5632002	2.3531	1935.1	10.20	1.812	14.82	13.24
(7*s*6*p*3*d*1*f*)	5	−75.5651210	2.3524	1940.3	10.15	1.813	14.73	13.31
(7*s*6*p*3*d*2*f*)	5	−75.5652052	2.3523	1939.7	10.25	1.813	14.77	13.30
STF[c]	5	−75.56515	2.3518	1939.8	10.29	1.814	15.04	13.29
		$C_2^-[^2\Pi_u(1\pi_u^3 3\sigma_g^2)]$						
(7*s*6*p*3*d*)	4	−75.5888509	2.4239	1853.9	9.049	1.708	13.63	12.15
(7*s*6*p*3*d*1*f*)	4	−75.5897963	2.4230	1858.3	9.142	1.709	13.59	12.21
(7*s*6*p*3*d*2*f*)	4	−75.5898776	2.4228	1858.3	9.209	1.709	13.61	12.21

[a] The units are: atomic units for E_T and r_e; cm^{-1} for ω_e, $\omega_e x_e$, and B_e; 1×10^{-3} cm^{-1} for α_e; $1 \times 10^{+5}$ dyne/cm for κ_e

[b] M denotes the method used to arrive at the values of spectroscopic constants: D = Dunham analysis; E = experimental; decimal digit = degree of polynomial used in fitting

[c] [11]

(by about 0.0001 a_0). Dupuis and Liu [11] used a fairly large STF (7*s*5*p*3*d*1*f*) basis set in studies on $C_2[^1\Sigma_g^+(1\pi_u^4 3\sigma_g^0)]$ and $C_2^-[^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)]$. We used their values of total energy in order to evaluate the values of spectroscopic constants which, virtually undistinguishable from our values, are given in Table 4. Dupuis and Liu built their basis set starting from an augmented basis set of Clementi and Roetti [12]; the exponential parameters of the most diffuse functions were then optimized in the molecular calculations. It is evident from Table 4 that their STF (*7s5p3d1f*) basis set is as good as out GTF (*7s6p3d1f*) basis, in which all exponents, except for that of *f* function, were optimized by minimizing the atomic total energy.

Compared with experiment [13], the ground states of both C_2 and C_2^- are incorrectly predicted on the Hartree–Fock level. The total energies of the states arising from the $1\pi_u^2 3\sigma_g^2$ valence configuration of C_2 fall below the energy of the experimentally determined ground state $^1\Sigma_g^+$; for the negative ion C_2^-, the $^2\Pi_u(1\pi_u^3 3\sigma_g^2)$ state has lower energy than the experimental ground state $^2\Sigma_g^+(1\pi_u^4 3\sigma_g^1)$. Inclusion of electron correlation is necessary to remedy the situation [14].

N_2, N_2^+, *and* N_2^-

The value of the exponential parameter of the single *f* function, $\zeta_f = 1.241$, was obtained by minimizing the total energy of $N_2[^1\Sigma_g^+]$ at $r = 2.068$ a_0. The same value was used in all calculations. The exponents of the two *f* functions were taken equal to the exponents ζ_{11} and ζ_{12} from the exponent pool (cf. Tables 1 and 2). The exponential parameter of the *g* function was set equal to that of the

Table 5. Total and orbital energies[a] and differences of total and orbital energies[b] for N_2, N_2^+, and N_2^- (in E_h)

Basis	E_T	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$
	$N_2[^1\Sigma_g^+(3\sigma_g^2 1\pi_u^4)]$			$r = 2.068$ a_0			
STF[c]	*−108.992800*	*−15.6820*	*−15.6783*	*−1.4736*	*−0.7780*	*−0.6350*	*−0.6154*
(*7s6p3d*)	0.003041	−0.0011	−0.0012	−0.0020	−0.0002	−0.0009	0.0002
(*7s6p3d1f*)	0.000058	0.0002	0.0001	0.0001	0.0001	0.0004	0.0000
(*7s6p3d2f*)	−0.000172	0.0002	0.0001	0.0001	0.0001	0.0004	0.0000
(*7s6p3d2f1g*)	−0.000470	0.0003	0.0002	0.0002	0.0001	0.0004	0.0000
NHF[d]	−0.001008	0.0001	0.0001	0.0002	−0.0001	0.0002	−0.0002
	$N_2^+[^2\Sigma_g^+(3\sigma_g^1 1\pi_u^4)]$			$r = 2.113$ a_0			
STF[c]	*−108.403700*	*−16.1827*	*−16.1800*	*−1.8807*	*−1.1569*	*−1.1235*	*−1.0237*
(*7s6p3d*)	0.004437	−0.0016	−0.0016	−0.0026	−0.0006	−0.0012	0.0002
(*7s6p3d1f*)	−0.000091	0.0000	0.0000	0.0001	−0.0001	0.0001	−0.0002
(*7s6p3d2f*)	−0.000318	0.0001	0.0001	0.0001	−0.0001	0.0001	−0.0002
(*7s6p3d2f1g*)	−0.000553	0.0002	0.0002	0.0002	−0.0001	0.0001	−0.0003
	$N_2^+[^2\Pi_u(3\sigma_g^2 1\pi_u^3)]$			$r = 2.222$ a_0			
STF[c]	*−108.427000*	*−16.1805*	*−16.1782*	*−1.8644*	*−1.2062*	*−1.0349*	*−1.0289*
(*7s6p3d*)	0.002678	−0.0011	−0.0011	−0.0021	−0.0003	−0.0010	0.0003
(*7s6p3d1f*)	−0.000064	0.0002	0.0002	0.0001	0.0000	0.0001	0.0000
(*7s6p3d2f*)	−0.000218	0.0003	0.0002	0.0002	0.0001	0.0002	0.0000
(*7s6p3d2f1g*)	−0.000369	0.0003	0.0003	0.0003	0.0001	0.0002	0.0000

[a] The STF reference values of total and orbital energies are printed in italic

[b] The differences of total and orbital energies are defined as E_T(basis) − E_T(STF reference)

[c] [5]

[d] [7]

Table 6. Spectroscopic constants[a] of N_2, N_2^+, and N_2^-

Basis	M[b]	E_T	r_e	ω_e	$\omega_e x_e$	B_e	α_e	κ_e
		$N_2[^1\Sigma_g^+(3\sigma_g^2 1\pi_u^4)]$						
$(7s6p1d)$[c]	4	−108.9856230	2.0167	2746.3	10.75	2.114	13.61	31.11
$(7s5p1d)$[d]	4	−108.9833634	2.0259	2723.5	10.14	2.095	13.30	30.60
$(7s6p2d)$[e]	4	−108.9910881	2.0152	2728.1	10.60	2.117	13.74	30.70
$(7s6p2d)$[f]	4	−108.9904493	2.0136	2732.6	10.69	2.121	13.74	30.80
$(7s6p3d)$	4	−108.9923890	2.0146	2723.5	10.66	2.118	13.83	30.60
$(7s6p3d1f)$	4	−108.9954254	2.0142	2730.8	10.69	2.119	13.75	30.76
$(7s6p3d2f)$	4	−108.9957090	2.0137	2731.7	10.78	2.120	13.77	30.78
$(7s6p3d2f1g)$	4	−108.9958633	2.0138	2730.7	10.73	2.120	13.77	30.76
STF[g]	D		2.0134	2729.6	8.378	2.121	13.47	30.73
		$N_2^+[^2\Sigma_g^+(3\sigma_g^1 1\pi_u^4)]$						
$(7s6p3d)$	4	−108.4033806	2.0410	2560.7	13.12	2.064	15.61	27.05
$(7s6p3d1f)$	4	−108.4079581	2.0408	2568.6	12.87	2.064	15.50	27.22
$(7s6p3d2f)$	4	−108.4082644	2.0401	2569.1	13.03	2.066	15.56	27.23
$(7s6p3d2f1g)$	4	−108.4084694	2.0403	2568.1	13.06	2.065	15.54	27.21
		$N_2^+[^2\Pi_u(3\sigma_g^2 1\pi_u^3)]$						
$(7s6p3d)$	4	−108.4292206	2.1352	2329.8	10.98	1.886	13.78	22.39
$(7s6p3d1f)$	4	−108.4321036	2.1343	2338.5	11.06	1.888	13.72	22.56
$(7s6p3d2f)$	4	−108.4322955	2.1339	2338.2	11.18	1.888	13.77	22.55
$(7s6p3d2f1g)$	4	−108.4324296	2.1340	2337.5	11.09	1.888	13.75	22.54

[a,b] See Table 4 for notation
[c] $\zeta_d = 1.034$ (optimized)
[d] $\zeta_d = 0.8055 \approx \zeta_{12}$
[e] $\{\zeta_d\} = \{1.542, 0.650\}$ (optimized)
[f] $\{\zeta_d\} = \{1.911, 0.8055\} \approx \{\zeta_{11}, \zeta_{12}\}$
[g] [16]

single *f* function ($\zeta_g = 1.241$). In Table 5 we compared the total and orbital energies with the results of the calculations done by Cade and Wahl, who used STF basis set [5], and with the results of the numerical Hartree–Fock (NHF) calculations done by Laaksonen et al. [7].

Addition of a single *f* function is necessary to secure convergence of the orbital energies. Except for $N_2[^1\Sigma_g^+(3\sigma_g^4 1\pi_u^2)]$, our GTF $(7s6p3d1f)$ basis gives the total energies slightly lower than the STF values of Cade and Wahl. The single *f* function improves the total energy by about 3 mE$_h$. Replacing the single *f* function by the set of two *f* functions (unoptimized exponents) lowers the total energy insignificantly, by less than 0.3 mE$_h$. Adding the single *g* function to the $(7s6p3d2f)$ improves the total energy by less than 0.3 mE$_h$. This still leaves a difference of 0.538 mE$_h$ between our best $(7s6p3d2f1g)$ result and the numerical Hartree–Fock value of the total energy. The difference may be diminished by about 0.16 mE$_h$ when a molecular-energy-optimized value of ζ_g is used. The atomic total energy of N(^4S) in the $(7s6p3d)$ basis, −54.400862 E$_h$ [3], is about 0.07 mE$_h$ above the Hartree–Fock value, −54.400934 E$_h$ [15]; therefore a major part of the remaining difference in the molecular total energies may be of atomic origin.

The values of the spectroscopic constants in Table 6 are close to the converged values already at the level of the $(7s6p3d)$ basis set. Addition of *f* functions always slightly shortens the bond length, while addition of the single *g* function leaves the bond length essentially unchanged. The differences between the (*7s6p3d2f1g*) values and the ones reported by Cade et al. [16] (especially for $\omega_e x_e$) may be attributed to different methods of analysing the potential energy curve.

For $N_2[^1\Sigma_g^+(3\sigma_g^2 1\pi_u^4)]$ we also tested performance of the (*7s6p*) basis set augmented with only one or two *d* functions, rather than with the three we routinely used. The single *d* function with $\zeta_d = 1.034$, optimized in molecular calculations, brings about errors of about 10 mE$_h$ in the total energy, 0.003 a$_0$ in r_e, and 26 cm^{-1} (or 1%) in the vibrational frequency. The results obtained with $\zeta_d = 0.8055$, taken out of the exponent pool, are worse: the total energy and r_e are further away from the converged values, while ω_e is closer to the best value. When two *d* functions are used the results are of good quality, regardless whether the values of the exponents were optimized in the molecular calculations or whether they were taken from the exponent pool; furthermore, the results are rather close to the best values.

O_2, O_2^+, *and* O_2^-

The value of the exponential parameter of the single *f* function was adjusted in the molecular calculations on $O_2[^3\Sigma_g^-(1\pi_u^4 1\pi_g^2)]$; the value $\zeta_f = 1.652$ was used in all calculations. Using the GTF (*7s6p3d1f*) basis set we obtain total energies better than the ones reported by Cade and Wahl (Table 7). Replacing the single *f* function with the set of two *f* functions results in improvement of the total energies by about 0.2 mE$_h$. The STF basis set of Cade and Wahl, optimized in O_2, is able to represent the wavefunction of O_2^- quite well, contrary to the situation found in C_2^- (cf. Table 3).

In the calculations on $O_2\ ^3\Sigma_g^-$ we added one *g* function to the (*7s6p3d2f*) basis. The total energy varied very slowly with the exponential parameter ζ_g of the (*7s6p3d2f1g*) basis set. For all calculations we adopted the value of $\zeta_g = 2.55$, close to ζ_{11}, which happens to give the total energy close to the best value. Taking into account the defect in the atomic total energy of about 0.11 mE$_h$, we may expect that the (*7s6p3d2f1g*) value is at least 0.5 mE$_h$ above the Hartree–Fock limit.

The behavior of the potential energy curves near minima (Table 8) is quite well represented with the (*7s6p3d*) basis set. Addition of the single *f* function improves the total energy by 3.3 to 5.7 mE$_h$; the bond lengths are shortened by about 0.04 a$_0$. Replacement of the single *f* function by two *f* functions lowers the total energy by about 0.2 mE$_h$ and increases the bond length by 0.0004 to 0.0009 a$_0$.

Replacing the three *d* functions with two *d* functions whose exponents (1.652 and 0.962) were adjusted in $O_2\ ^3\Sigma_g^-$ calculations at $r = 2.282$ a$_0$ results only in minor deterioration of results, uniform for all systems. However, using only one *d* function causes significant worsening of results; furthermore, some systems (e.g., O_2^+) are affected more than others.

Table 7. Total and orbital energies[a] and differences of total and orbital energies[b] for O_2, O_2^+, and O_2^- (in E_h)

Basis	E_T	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$	$1\pi_g$
	$O_2[^3\Sigma_g^-(1\pi_u^4 1\pi_g^2)]$				$r = 2.282\ a_0$			
STF[c]	*−149.665900*	*−20.7296*	*−20.7286*	*−1.6488*	*−1.0987*	*−0.7358*	*−0.7052*	*−0.5319*
(*7s6p3d*)	0.003394	−0.0013	−0.0014	−0.0025	−0.0008	−0.0014	0.0000	−0.0007
(*7s6p3d1f*)	−0.000504	−0.0003	−0.0003	−0.0006	−0.0003	−0.0001	−0.0003	−0.0004
(*7s6p3d2f*)	−0.000721	−0.0002	−0.0003	−0.0005	−0.0002	0.0000	−0.0003	−0.0004
(*7s6p3d2f1g*)	−0.001019	−0.0002	−0.0002	−0.0004	−0.0002	0.0000	−0.0004	−0.0003
	$O_2[^1\Delta_g(1\pi_u^4 1\pi_g^2)]$				$r = 2.297\ a_0$			
STF[c]	*−149.617200*	*−20.7388*	*−20.7378*	*−1.6468*	*−1.1054*	*−0.7375*	*−0.7058*	*−0.4893*
(*7s6p3d*)	0.003400	−0.0010	−0.0010	−0.0022	−0.0017	−0.0015	0.0003	−0.0005
(*7s6p3d1f*)	−0.000373	0.0000	0.0000	−0.0003	−0.0002	−0.0002	0.0000	−0.0002
(*7s6p3d2f*)	−0.000602	0.0001	0.0000	−0.0002	−0.0001	−0.0001	0.0000	−0.0001
	$O_2[^1\Sigma_g^+(1\pi_u^4 1\pi_g^2)]$				$r = 2.318\ a_0$			
STF[c]	*−149.568300*	*−20.7483*	*−20.7473*	*−1.6418*	*−1.1132*	*−0.7387*	*−0.7048*	*−0.4487*
(*7s6p3d*)	0.003336	−0.0010	−0.0011	−0.0024	−0.0007	−0.0014	0.0001	−0.0007
(*7s6p3d1f*)	−0.000346	0.0000	−0.0001	−0.0006	−0.0001	0.0000	−0.0002	−0.0004
(*7s6p3d2f*)	−0.000599	0.0000	−0.0001	−0.0004	−0.0001	0.0002	−0.0002	−0.0003
	$O_2^+[^2\Pi_g(1\pi_u^4 1\pi_g^1)]$				$r = 2.122\ a_0$			
STF[c]	*−149.225700*	*−21.2705*	*−21.2689*	*−2.2236*	*−1.5266*	*−1.2320*	*−1.1901*	*−0.9688*
(*7s6p3d*)	0.004024	−0.0016	−0.0015	−0.0028	−0.0006	−0.0015	0.0004	−0.0008
(*7s6p3d1f*)	−0.001049	0.0000	0.0001	0.0000	0.0001	0.0002	0.0001	−0.0001
(*7s6p3d2f*)	−0.001254	0.0001	0.0001	0.0002	0.0001	0.0002	0.0002	0.0000
	$O_2^-[^2\Pi_g(1\pi_u^4 1\pi_g^3)]$				$r = 2.400\ a_0$			
STF[c]	*−149.642700*	*−20.2877*	*−20.2871*	*−1.1865*	*−0.7260*	*−0.3150*	*−0.3062*	*−0.0888*
(*7s6p2d*)	0.001724	−0.0066	−0.0065	−0.0060	−0.0044	−0.0046	−0.0033	−0.0030
(*7s6p3d*)	0.001355	−0.0065	−0.0065	−0.0060	−0.0045	−0.0047	−0.0033	−0.0030
(*7s6p3d1f*)	−0.001873	−0.0058	−0.0058	−0.0047	−0.0040	−0.0036	−0.0037	−0.0029
(*7s6p3d2f*)	−0.002117	−0.0058	−0.0058	−0.0046	−0.0040	−0.0035	−0.0037	−0.0028

[a] The STF reference values of total and orbital energies are printed in italic

[b] The differences of total and orbital energies are defined as E_T(basis) − E_T(STF reference)

[c] [5]

CO, CO^+, CO^{2+}, *and* CO^-

As mentioned in the Introduction, the STF results of Cade and Huo [6] for heteronuclear diatomics are of poorer quality due to basis set incompleteness. This is manifested in Table 9, where already our (*7s6p3d*) basis set gives better total energies. Using a large STF (*6s4p1d1f*) basis Green [17] obtained $-112.78924\ E_h$ for the total energy of CO at $r = 2.132\ a_0$ (the improvement of $0.13\ mE_h$ over the result of McLean and Yoshimine [18] was due to a larger σ space used by Green).

Table 8. Spectroscopic constants[a] of O_2, O_2^+, and O_2^-

Basis	M[b]	E_T	r_e	ω_e	$\omega_e x_e$	B_e	α_e	κ_e
		$O_2[{}^3\Sigma_g^-(1\pi_u^4 1\pi_g^2)]$						
$(7s6p1d)$[c]	5	−149.6637252	2.1847	2010.5	9.664	1.577	12.27	19.05
$(7s6p2d)$[d]	5	−149.6676143	2.1789	2003.5	9.557	1.585	12.22	18.91
$(7s6p3d)$	5	−149.6682237	2.1787	1999.2	9.385	1.586	12.11	18.83
$(7s6p3d1f)$	5	−149.6726217	2.1747	2011.5	9.413	1.592	12.17	19.07
$(7s6p3d2f)$	5	−149.6727743	2.1750	2006.5	9.245	1.591	12.14	18.97
		$O_2[{}^1\Delta_g(1\pi_u^4 1\pi_g^2)]$						
$(7s6p1d)$[c]	5	−149.6165347	2.1854	2000.7	9.678	1.576	12.33	18.86
$(7s6p2d)$[d]	5	−149.6204022	2.1797	1993.5	9.566	1.584	12.28	18.73
$(7s6p3d)$	5	−149.6210123	2.1795	1989.4	9.408	1.585	12.17	18.65
$(7s6p3d1f)$	5	−149.6253462	2.1754	2001.6	9.438	1.591	12.23	18.88
$(7s6p3d2f)$	5	−149.6254988	2.1758	1996.5	9.269	1.590	12.20	18.78
		$O_2[{}^1\Sigma_g^+(1\pi_u^4 1\pi_g^2)]$						
$(7s6p1d)$[c]	5	−149.5701386	2.1858	1991.7	9.699	1.576	12.40	18.69
$(7s6p2d)$[d]	5	−149.5740015	2.1800	1984.2	9.583	1.584	12.34	18.55
$(7s6p3d)$	5	−149.5746154	2.1798	1980.2	9.427	1.584	12.24	18.48
$(7s6p3d1f)$	5	−149.5789446	2.1757	1992.5	9.573	1.590	12.30	18.71
$(7s6p3d2f)$	5	−149.5791022	2.1761	1987.1	9.290	1.590	12.27	18.61
		$O_2^+[{}^2\Pi_g(1\pi_u^4 1\pi_g^1)]$						
$(7s6p1d)$[c]	5	−149.2249432	2.0115	2519.0	11.38	1.860	13.34	29.90
$(7s6p2d)$[d]	5	−149.2319057	2.0045	2502.7	10.93	1.873	13.47	29.51
$(7s6p3d)$	5	−149.2331056	2.0033	2495.1	10.88	1.876	13.45	29.34
$(7s6p3d1f)$	5	−149.2388092	2.0007	2511.8	11.02	1.881	13.47	29.73
$(7s6p3d2f)$	5	−149.2390144	2.0004	2507.4	11.04	1.881	13.58	29.62
		$O_2^-[{}^2\Pi_g(1\pi_u^4 1\pi_g^3)]$						
$(7s6p1d)$[c]	5	−149.6392860	2.4292	1451.0	7.447	1.276	11.11	9.921
$(7s6p2d)$[d]	5	−149.6411585	2.4237	1446.0	7.495	1.281	11.27	9.852
$(7s6p3d)$	5	−149.6415377	2.4230	1450.4	7.615	1.282	11.14	9.913
$(7s6p3d1f)$	5	−149.6446755	2.4176	1459.5	7.497	1.288	11.08	10.04
$(7s6p3d2f)$	5	−149.6449314	2.4187	1457.4	7.414	1.287	10.98	10.01

[a,b] See Table 4 for notation

[c] $\zeta_d = 1.07 \approx \zeta_{12}$

[d] $\{\zeta_d\} = \{1.652, 0.692\}$ (adjusted in molecular calculations)

Table 9. Total and orbital energies[a] and differences of total and orbital energies[b] for CO, CO^+, CO^{2+}, and CO^- (in E_h)

Basis	E_T	1σ	2σ	3σ	4σ	1π	5σ
	$CO[{}^1\Sigma^+(1\pi^4 5\sigma^2)]$			$r = 2.132\ a_0$			
STF[c]	*−112.786000*	*−20.6612*	*−11.3593*	*−1.5192*	*−0.8024*	*−0.6377*	*−0.5530*
$(7s6p3d)$	−0.001066	−0.0030	−0.0029	−0.0038	−0.0029	−0.0023	−0.0026
$(7s6p3d1f)$	−0.003998	−0.0034	−0.0010	−0.0025	−0.0021	−0.0026	−0.0019
$(7s6p3d2f)$	−0.004165	−0.0034	−0.0010	−0.0025	−0.0021	−0.0026	−0.0019
STF[d]	−0.003240	−0.0038	−0.0007	−0.0018	−0.0016	−0.0023	−0.0010
NHF[e]	−0.004950	−0.0033	−0.0007	−0.0023	−0.0021	−0.0027	−0.0019

Table 9 (continued)

Basis	E_T	1σ	2σ	3σ	4σ	1π	5σ
	$CO^+[^2\Sigma^+(1\pi^4 5\sigma^1)]$			$r = 2.107\ a_0$			
STF[c]	*−112.291500*	*−21.0851*	*−11.8654*	*−1.9217*	*−1.1658*	*−1.0214*	*−1.1222*
(*7s6p3d*)	−0.005729	0.0098	0.0095	0.0096	0.0086	0.0076	0.0042
(*7s6p3d1f*)	−0.009238	0.0111	0.0111	0.0116	0.0100	0.0071	0.0052
(*7s6p3d2f*)	−0.009411	0.0111	0.0112	0.0117	0.0100	0.0071	0.0052
	$CO^+[^2\Pi(1\pi^3 5\sigma^2)]$			$r = 2.350\ a_0$			
STF[c]	*−112.230400*	*−21.1442*	*−11.8647*	*−1.9008*	*−1.2269*	*−1.0773*	*−0.9438*
(*7s6p3d*)	−0.007799	0.0117	0.0103	0.0112	0.0099	0.0092	0.0060
(*7s6p3d1f*)	−0.010249	0.0127	0.0116	0.0126	0.0109	0.0088	0.0065
(*7s6p3d2f*)	−0.010434	0.0127	0.0116	0.0127	0.0110	0.0088	0.0066
	$CO^{2+}[^1\Sigma^+(1\pi^4 5\sigma^0)]$			$r = 2.132\ a_0$			
STF[c]	*−111.228900*	*−21.5893*	*−12.4743*	*−2.3584*	*−1.5716*	*−1.4466*	
(*7s6p3d*)	−0.014408	0.0129	0.0246	0.0160	0.0143	0.0098	
(*7s6p3d1f*)	−0.019163	0.0139	0.0268	0.0182	0.0157	0.0089	
(*7s6p3d2f*)	−0.019350	0.0139	0.0269	0.0183	0.0157	0.0089	

[a] The STF reference values of total and orbital energies are printed in italic

[b] The differences of total and orbital energies are defined as E_T(basis) − E_T(STF reference)

[c] [6]

[d] [17]

[e] [7]

In the calculations with a single *f* function at each atom we used the values of the exponential parameters which had been optimized in the corresponding homonuclear molecules, namely $\zeta_f = 1.0847$ for carbon and $\zeta_f = 1.6520$ for oxygen. The presence of a single *f* function improves the total energy by 2.4 to 4.8 mE_h. Using the values of exponents optimized by minimizing the total energy of CO results in an insignificant improvement of the energy by about 0.049 mE_h. Two *f* functions cause an additional energy gain of about 0.2 mE_h.

While the values of the orbital energies of CO $^1\Sigma^+$ are close to the results of the numerical Hartree–Fock calculations [7], the error in total energy is still about 0.79 mE_h. This discrepancy will be significantly reduced if one *g* function is added and the Hartree–Fock atomic basis set is used. Feller et al. [19] used a large GTF (*19s10p4d2f*) basis set contracted to (*10s6p4d2f*) to obtain the total energy of −112.7903 E_h.

The values of the spectroscopic constants are compared in Table 10 with the ones derived from the results of McLean and Yoshimine [18] and the ones reported by Huo [20]. The agreement is very good; the smaller number of points on the McLean and Yoshimine's potential energy curve as well as their distribution around the minimum affect the values of ω_e and $\omega_e x_e$. As in the previous cases, the (*7s6p3d*) basis provides results fairly close to the best data.

Table 10. Spectroscopic constants[a] of CO, CO^+, CO^{2+}, and CO^-

Basis	M[b]	E_T	r_e	ω_e	$\omega_e x_e$	B_e	α_e	κ_e
		CO[$^1\Sigma^+(1\pi^4 5\sigma^2)$]						
(7*s*6*p*3*d*)	6	−112.7887513	2.0836	2424.8	12.70	2.022	15.19	23.75
(7*s*6*p*3*d*1*f*)	6	−112.7917297	2.0830	2429.1	11.25	2.024	15.07	23.84
(7*s*6*p*3*d*2*f*)	6	−112.7919103	2.0828	2427.7	11.38	2.024	15.09	23.81
STF[c]	4	−112.7908542	2.0832	2445.1	13.60	2.023	15.33	24.15
STF[d]	D		2.081	2431.0	11.69	2.027	15.25	23.86
		CO^+[$^2\Sigma^+(1\pi^4 5\sigma^1)$]						
(7*s*6*p*3*d*)	6	−112.3014519	2.0350	2619.1	13.19	2.120	15.59	27.71
(7*s*6*p*3*d*1*f*)	5	−112.3049901	2.0349	2622.9	13.10	2.120	15.52	27.79
(7*s*6*p*3*d*2*f*)	5	−112.3051819	2.0346	2621.1	13.08	2.121	15.53	27.75
		CO^+[$^2\Pi(1\pi^3 5\sigma^2)$]						
(7*s*6*p*3*d*)	5	−112.2395814	2.2898	1778.2	11.76	1.675	16.98	12.77
(7*s*6*p*3*d*1*f*)	5	−112.2421317	2.2879	1788.2	11.69	1.677	16.82	12.92
(7*s*6*p*3*d*2*f*)	5	−112.2423046	2.2881	1786.0	11.72	1.677	16.85	12.89
		CO^{2+}[$^1\Sigma^+(1\pi^4 5\sigma^0)$]						
(7*s*6*p*3*d*)	5	−111.2490455	2.0404	2463.6	26.56	2.109	22.64	24.52
(7*s*6*p*3*d*1*f*)	5	−111.2537301	2.0410	2463.3	26.56	2.108	22.57	24.51
(7*s*6*p*3*d*2*f*)	5	−111.2539283	2.0408	2461.1	26.63	2.108	22.63	24.47

[a,b] See Table 4 for notation

[c] [18]

[d] [20]

Conclusions

The present study indicates that moderately large Gaussian basis sets, used without reoptimization of exponents in molecular calculations, are capable of surpassing the Slater-type basis sets whose exponents were optimized in molecular environment. The Gaussian basis sets work especially well for the ionized species. Their flexibility is achieved due to the large number of primitive Gaussian functions which are deployed in the valence region; the same flexibility may be achieved in Slater-type basis sets provided a large number of functions is used. Thus, until a computationally fast algorithm for the evaluation of molecular integrals over Slater-type functions is developed, Gaussian-type functions will remain the preferred basis functions for molecular calculations.

The present Gaussian basis sets still have to be improved if better agreement with the numerical Hartree–Fock results is sought. According to the results for the molecular ground states we deduce that the (*MsNp*) basis sets have to be augmented by three *d*, two *f*, and one *g* functions to enable approaching near-Hartree–Fock quality for the wavefunction. The judgment about performance of the present basis sets in calculations for excited states will have to be deferred until corresponding numerical Hartree–Fock results become available.

The set of three *d* and two *f* functions (cf. Table 1) provide the diverse exponents needed to adequately span the σ and π spaces without the need for exponent reoptimization. Furthermore, such a large set of auxiliary functions may be required in order to avoid the differential effects which arise when a single function, optimized in molecular calculations at a fixed internuclear distance, is used at other molecular geometries. Results for O_2 and N_2 seem to indicate that for rudimentary studies on molecular geometries, the $(7s6p2d)$ basis set may provide results of acceptably good quality.

The accurate, near-Hartree–Fock wavefunctions which may be obtained with the primary $(7s6p)$ basis sets constitute a reliable starting point for post-Hartree–Fock studies which are clearly needed whenever, as in many of the cases studied here, the ground states are incorrectly identified and molecular geometries are incorrectly predicted at the Hartree–Fock level. However, in the calculations involving electron correlation, the correlating functions should include more than the few *d*, *f*, and *g* functions which were found to be adequate for the SCF wavefunction [21, 22].

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References

1. Huzinaga S, Klobukowski M (1988) J Mol Struct (Theochem) 167:1
2. Huzinaga S, Klobukowski M (1985) Chem Phys Lett 120:509
3. Dingle T, Huzinaga S, Klobukowski M (1989) J Comput Chem 10:753
4. Klobukowski M, Huzinaga S (1986) J Chem Phys 84:323
5. Cade PE, Wahl AC (1974) At Data Nucl Data Tables 13:339
6. Cade PE, Huo WM (1975) At Data Nucl Data Tables 14:1
7. Sundholm D, Pyykkö P, Laaksonen L (1985) Mol Phys 56:1411; Laaksonen L, Pyykkö P, Sundholm D (1986) Comput Phys Reports 4:1313
8. Müller-Platte F: private communication
9. King H, Dupuis M, Rys J (1980) Nat Resour Comput Chem Software Cat, program no QH07, vol 1
10. Carbó R, Riera JM (1978) A general SCF theory. (Lect Notes Chem, vol 5) Springer, Berlin Heidelberg New York
11. Dupuis M, Liu B (1980) J Chem Phys 73:337
12. Clementi E, Roetti C (1974) At Data Nucl Data Tables 14:177
13. Radzig AA, Smirnov BM (1985) Reference data on atoms, molecules, and ions (Springer Series Chem Phys, vol 31) Springer, Berlin Heidelberg New York
14. Hurley AC (1976) Electron correlation in small molecules. Academic Press, London
15. Froese-Fischer C (1977) The Hartree–Fock method for atoms. Wiley, New York
16. Cade PE, Sales KD, Wahl AC (1966) J Chem Phys 44:1973
17. Green S (1970) J Chem Phys 52:3100
18. McLean AD, Yoshimine M (1967) Tables of linear molecule wave functions. IBM, San Jose; Int J Quantum Chem 1:313
19. Feller D, Boyle CM, Davidson ER (1987) J Chem Phys 86:3424
20. Huo WM (1965) J Chem Phys 43:624
21. Jankowski K, Becherer R, Scharf P, Schiffer H, Ahlrichs R (1985) J Chem Phys 82:1413
22. Almlöf J, Taylor PR (1987) J Chem Phys 86:4070