

GAUSSIAN BASIS SET FOR SODIUM COMPATIBLE WITH THE DUNNING'S BASIS SETS FOR THE FIRST ROW ATOMS

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A contracted [7s4p] basis set for sodium is suggested which is compatible with the Dunning's basis sets for the first row atoms. The basis set is employed in the SCF calculations on NaH and NaLi. Calculated optimum interatomic distances, vibrational frequencies, dissociation energies, and some one-electron properties are compared with the results of published near Hartree-Fock calculations.

In preparation for an *ab initio* study of the $\text{Na} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}$ equilibrium, we encountered a problem in the selection of a basis set for sodium. We looked for a basis set which would be compatible with the currently used Dunning's basis sets of the "double zeta" quality for the first row atoms^{1,2}. In searching for such a basis set, we took into account the statement of Schaefer³ that if minimum or double zeta basis sets are to be used for sodium, the 3s-3p near degeneracy should be recognized and a 3p function added to the basis set. The second guidance in the choice of the basis set was the opinion of Veillard⁴ that a basis set for a second row atom, compatible with the (10s6p) basis sets of Huzinaga⁵ for the first row atoms should be of the (12s9p) size; the two additional s-type functions being a representation of the 3s atomic orbital and the three additional p-type functions being a representation of the 3p atomic orbital. Since the 3p atomic orbital of Na may be taken as a polarization function rather than a part of the valence shell, we think that it is sufficient to use only one or two additional p-type functions. Hence, for the basis set to be compatible with the Dunning's (9s5p)/[4s2p] basis sets¹, it should be of the (11s7p)/[6s4p] size. In the literature⁶, we located a basis set just of this type. However, the authors of the paper⁶ gave no specification of the contraction and their reference to the (11s7p) primitive set is probably wrong, since in the cited paper of Huzinaga⁷ we found no mention of the (11s7p) basis set. Among the other basis sets reported in the literature, the (10s6p) basis set of Roos and Siegbahn⁸ was for our purposes too small. The (17s12p) basis set of Huzinaga and Sakai⁷ was too large and overcontracted to [4s2p]. We decided therefore to develop our own basis set.

Basis Set Optimization

The starting point was the (12s6p) primitive set of Veillard⁴. On the basis of results of the Dunning's study⁹ of the chlorine basis set contraction, we examined two

contractions of the *s*-set: (5,1,2,1,1,1,1) and (6,1,1,1,1,1,1). The ratio of the expansion coefficients of the 7th and 8th functions in the 1*s* atomic orbital of Na is of the opposite sign than when it is in the 2*s* atomic orbital⁴. Hence grouping of the two functions means violation of the Dunning's^{1,9} "rule B" and the (5,1,2,1,1,1,1) contraction should be inferior to the (6,1,1,1,1,1,1) contraction which satisfies both the rules "A" and "B". For the *p*-set we considered a single contraction (4,1,1). The two resulting [7*s*3*p*] basis sets were tested on Na and NaH. For hydrogen, we used the Dunning's scaled (4*s*)/[2*s*] basis set¹. The interatomic distance* Na—H was $R = 3.62811$. We obtained the following energies*: -161.844232 for Na(²S) and -162.363479 for NaH if the (5,1,2,1,1,1,1) contraction of the *s*-set was used and -161.843496 for Na(²S) and -162.362637 for NaH if the (6,1,1,1,1,1,1) contraction of the *s*-set was used. Surprisingly, lower energies were calculated with the (5,1,2,1,1,1,1) set. This fact was not examined in more detail, but the (6,1,1,1,1,1,1) set was abandoned in the next basis optimization. The energy⁴ of Na(²S) in the uncontracted (12*s*6*p*) set is -161.85259 .

For molecular calculations, the basis set at this stage was still deficient in the representation of *p* functions. The (6*p*) set of Veillard is in fact the expansion of the 2*p* atomic orbital. To enhance the participation of the 3*p* atomic orbital in chemical bonding, we augmented the basis set by a set (*p_x*, *p_y*, *p_z*) of diffuse *p* functions. Their exponent was optimized for the lowest ²*P* excited state of the Na atom and for NaH. The result is presented in Fig. 1. The optimum exponents 0.0351 and 0.05 give the energies -161.768163 and -162.373510 , respectively. For the standard value of the exponent, we selected the intermediate value of 0.04. The final basis set is presented in Table I. The ground state Na(²S) energy in this basis set is -161.844491 , compared with the Hartree-Fock limit¹⁰ -161.85890 .

Test Calculations on NaH and NaLi

To determine the effectiveness of the [7*s*4*p*] basis set, we performed the calculations on NaH and NaLi and compared them with reported near Hartree-Fock calculations¹¹⁻¹³ for which the total energies were estimated to lie only about 0.001 above the Hartree-Fock limit. For hydrogen we used the Dunning's scaled (4*s*)/[2*s*] set¹ and for lithium the (9*s*4*p*)/[4*s*2*p*] set of Pearson and coworkers¹⁴ was employed. Our computed SCF energy for NaH at a bond distance of 3.566 is -162.37319 , which is compared with Cade and Huo's near Hartree-Fock energy¹¹ of -162.3928 .

* If not otherwise noted the so called "atomic units" are used throughout. In order to agree with the International System of Units, we treat all quantities as relative dimensionless quantities. For example, to energy and distance we give the meaning E/e_0 and R/a_0 , where $e_0 = 2625.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $a_0 = 0.52917 \cdot 10^{-10} \text{ m}$. For conversion factors of the less common quantities see ref.¹⁶

TABLE I
Basis Set for Sodium

s-Set		p-Set	
Exponents	coefficients	exponents	coefficients
36 631.1	0.00038	148.928	0.00513
5 385.07	0.00305	34.5149	0.03791
1 216.20	0.01599	10.6045	0.15341
339.529	0.06427	3.67106	0.35313
109.563	0.19481	1.28490	1.00000
38.7834	1.00000	0.430941	1.00000
14.5790	0.39267	0.04	1.00000
5.27901	0.08282		
1.82902	1.00000		
0.620535	1.00000		
0.058065	1.00000		
0.024617	1.00000		

For NaLi at $R = 5.75$, we obtained the total energy of -169.27746 , compared with a value of -169.29291 reported by Bertoni and collaborators¹³. The utility of the basis set may however be best recognized from calculated molecular properties. In Tables II–V, we compare some computed spectroscopic and one-electron properties with published near Hartree–Fock data. Among the computed NaH one-

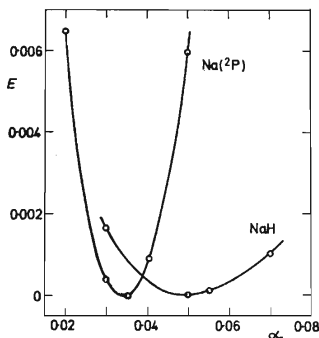


FIG. 1

Dependence of the Total Energy on the Exponent of the Most Diffuse p -Function in the $[7s4p]$ Basis Set

Relative energy scale is used with respect to the minima. The Na–H distance was kept at $R = 3.62811$. The Dunning's scaled $(4s)/[2p]$ basis set for hydrogen was used.

TABLE II
Spectroscopic Constants for NaH

Data	R_e^a	D_e, eV^b	ω_e, cm^{-1}	B_e, cm^{-1}
[7s4p] Set for Na (quadratic fit)	3.600	0.845	1 166	4.811
Near Hartree-Fock ^c (Dunham analysis)	3.616	0.934	1 187	4.766
Experiment ^d	3.566	2.3	1 172	4.901

^a Relative values, see footnote on p. 1461; ^b For $R = 3.566$; comparison with the experimental dissociation energy is meaningless because of the neglect of correlation energy in the SCF calculations; ^c ref.¹¹; ^d For references see the cited paper¹¹.

TABLE III
NaH One-Electron Properties^a: Dipole Moment, Charge Densities at Nuclei and Forces on Atoms

Data	μ	q_H	q_{Na}	F_H	F_{Na}
[7s4p] Set for Na	-2.724	0.3018	805.117	+0.0414	+0.5328
Near Hartree-Fock ^b	-2.739	0.3579	833.399	+0.0002	-0.0582

^a All entries refer to the interatomic distance $R = 3.566$ and have the meaning of relative quantities (see footnote on p. 1461); ^b ref.¹².

TABLE IV
Spectroscopic Constants for NaLi

Data	R_e^a	D_e, eV	ω_e, cm^{-1}	B_e, cm^{-1}
[7s4p] Set for Na	5.697 ^b	0.0461	238.7 ^b	0.3479
Near Hartree-Fock ^c (Dunham analysis)	5.6473	0.0763	250.65	0.34896

^a Relative values, see footnote on p. 1461; ^b From a quadratic fit; ^c ref.¹³.

-electron properties (Table III), the forces on atoms are the most divergent from near Hartree-Fock results. For the exact Hartree-Fock function at the Hartree-Fock equilibrium geometry, the Hellmann-Feynman force on each atom is zero¹⁵. With basis sets of a size similar to the basis set used in this paper, forces of about 0.5 are currently obtained. For NaLi, the total force is rather small. Some other properties, *e.g.* $(1/r)$ and (r^2) differ only slightly from the near Hartree-Fock results. These are, however, quantities that are a rather insensitive test of the accuracy of the wave function. With the other one-electron properties, the differences from the near Hartree-Fock values are of the same magnitude or less than may be expected for a basis set of the double zeta quality¹⁷.

It may be concluded that the overall agreement between the results given by the two basis sets is good and that the sodium $[7s4p]$ set gives a good account of both the energy and the wave function.

TABLE V

NaLi One-Electron Properties^a

Property	Contribution	[7s4p] Set for Na	Near Hartree-Fock ^b
$(1/r)_{\text{Na}}$	nuclear	+ 0.522	
$(1/r)_{\text{Na}}$	electronic	- 35.943	- 35.965
$(r^2)_{\text{Na}}$	nuclear	+ 99.187	
$(r^2)_{\text{Na}}$	electronic	- 136.261	- 135.69
$(z^2)_{\text{Na}}$	nuclear	+ 99.187	
$(z^2)_{\text{Na}}$	electronic	- 104.516	- 105.57
$(1/r)_{\text{Li}}$	nuclear	+ 1.913	
$(1/r)_{\text{Li}}$	electronic	- 7.651	- 7.651
$(r^2)_{\text{Li}}$	nuclear	+ 363.687	
$(r^2)_{\text{Li}}$	electronic	- 397.670	- 395.47
$(z^2)_{\text{Li}}$	nuclear	+ 363.687	
$(z^2)_{\text{Li}}$	electronic	- 365.925	- 365.35
μ	total	+ 0.269	+ 0.410
Q_{zz} ^c	total	11.265	9.772
F_{Na}	total	- 0.220	
F_{Li}	total	0.060	

^a All entries refer to the interatomic distance $R = 5.75$ and have the meaning of relative quantities (see footnote on p. 1461); ^b ref.¹³; ^c Relative to the centre of mass of $^{23}\text{Na}^7\text{Li}$; if Li is positioned in the origin and Na in the positive direction of the z axis, the centre of mass lies in the point (0.0; 0.0; 4.4083).

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