Near-Minimum Basis Set SCF Calculations on HCl as a Source of Transferable Parameters

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Ab initio LCAO-MO-SCF calculations on HCl yield an optimum exponent of 1.93 for $3d$ Slater-type orbitals with a single radial function when best atom exponents are used for the minimum basis set orbitals of chlorine and 1.2 is used for the $1s$ orbital of hydrogen. Hamiltonian matrix elements and other theoretical parameters which are used in approximate MO calculations on large molecules are tabulated. One-electron properties and electron density contour maps are compared to those computed from other wave functions. The accumulation of electrons in the A–H bonds, as well as the occupation of the $3d$ orbitals, decreases through the isoelectronic series SiH_4, PH_3, H_2S, HCl.

Ab initio LCAO-MO-SCF-Rechnungen für HCl ergeben einen optimalen Exponenten von 1,93 für $3d$-Slaterorbitale mit einer einzigen Radialfunktion, wenn gleichzeitig beste Atomexponenten für den minimalen Basissatz am Chloratom und 1,2 als Exponent für die $1s$-Orbitale am Wasserstoffatom angenommen werden. Die Hamilton-Matrixelemente und andere theoretische Parameter, die bei Näherungs-MO-Rechnungen an großen Molekülen gebraucht werden, sind tabelliert. Ein-Elektron-Eigenschaften und Elektronendichte-Diagramme werden mit solchen aus anderen Rechnungen verglichen. Die Konzentration von Elektronen in den A–H-Bindungen sowie die Besetzung der $3d$-Orbitale nimmt in der isoelektrischen Reihe SiH_4, PH_3, H_2S, HCl ab.

Calculs ab-initio LCAO-MO-SCF sur HCl donnant un exposant optimal de 1,93 pour les orbitales $3d$ de Slater a fonction radiale unique lorsque l'on utilise les meilleurs exposants pour la base minimale du chlore et 1,2 pour l'orbitale $1s$ de l'hydrogène. Les éléments de matrice hamiltoniens et les autres paramètres théoriques utilisés dans les calculs approchés sur les grandes molécules ont été tabulés. Les propriétés monoélectroniques et les cartes de densité électronique sont comparés à ceux obtenus à l'aide d'autres fonctions d'onde. L'accumulation des électrons dans les liaisons A–H, et l'occupation des orbitales $3d$, décroît le long de la série isoélectronique SiH_4, PH_3, H_2S et HCl.

Introduction

Two *ab initio* approaches have been used to obtain quantitative information on the extent and character of $3d$ orbital participation in bonds involving second-row elements, such as Si, P, S, and Cl. One such approach [1–3] has been to do LCAO-MO-SCF calculations on molecules, but, in order to be tractable, the molecules selected are usually diatomics or small polyatomics, and the basis sets are rather small, namely, the minimum basis sets of Slater-type orbitals together with the $3d$ orbitals of the heavy atom. These basis sets are inadequate for the purpose of obtaining Hartree-Fock descriptions of the molecules in question, but they are appropriate for obtaining theoretical parameters for transferal [1–4] to larger molecules of chemical and biological interest. By optimizing the $3d$ orbital exponent of a Slater-type orbital in SCF calculations on a small molecule, one has a first approximation for the value of the exponent in other bonding situations. The second theoretical approach to judging the contribution of $3d$ orbitals in chemical bonding is to carry out SCF calculations on the second-row atoms in

configurations which may simulate the state of the atom in a molecular environment [5–7]. These calculations are relatively simple because they avoid the evaluation of multicenter integrals.

Whereas the results of the first (molecular) approach are limited by their dependence on the basis functions, the second approach is attempting to extrapolate from atomic valence states to molecules. Yet current thinking from both approaches is that the $3d$ orbitals are of an appropriate size and energy for contributing to some observable properties of certain second-row molecules and that theoretical treatments of these molecules must invoke d orbital participation. Of course, calculations on molecules containing the second-row atom in a high valence state are very desirable, but such *ab initio* work is only now becoming available [8]. Full optimization of the basis sets in these calculations will lead toward the final resolution of the question of d orbital participation. The myriad of physical observables associated with the occupation of the $3d$ AO's in both ground and excited state molecules need not be discussed here (see, for example, [6, 9]).

The present investigation attempts to provide theoretical parameters which may be appropriate for chlorine $3d$ orbitals in a molecular environment. These parameters include the SCF Hamiltonian matrix elements, which may be used in the construction of Hamiltonian matrices for related, chlorine-containing molecules [4]. In addition, the optimized value of the Cl $3d$ exponent is reported, and a prediction [10] about its value is verified. The computed wave function of HCl is used to make interesting comparisons with existing ones for other second-row hydrides [1, 3, 11] and with published [11, 12] wave functions of HCl involving larger basis sets.

Calculations and Energetic Results

The near-minimum basis set SCF calculations, which were carried out with computer programs described elsewhere [13], on ground state ($^1\Sigma^+$) HCl at an experimental internuclear distance of 2.4087 a.u. [14] yield the results given in Tables 1 and 2. During the optimization of the $3d$ orbital exponent the minimum basis set exponents of Cl were held fixed at the best atom values [15] (2.0387 for $3p$), and the exponent of 1.20 chosen for the H $1s$ orbital was judged on the basis of earlier work to be nearly optimal [1, 3]. Since the $3d$ exponent will depend on the other exponents, the latter were specifically chosen because of their wide usage in semiempirical MO calculations on large molecules. Similar reasoning led us to optimize the exponent of the $3d$ orbitals ($3d_{z^2}$, $3d_{xz}$, $3d_{yz}$ with the molecule on the z axis) isotropically in order that a single value would be obtained for use in large asymmetric molecules. The optimum $3d$ exponent of 1.93 is in line with the observation [10] that the electrons in the $3d$ orbitals are subject to an effective nuclear charge only slightly diminished from that felt by the $3s$ and $3p$ electrons.

The total energy of HCl (Table 1) is poorer than that obtained with much larger basis sets by as much as 1 a.u., but as in the case of H_2S and SiH_4 [3], the near-minimum basis set gives a better energy than that obtained in the early one-center basis set calculations [12].

In studies of appropriate expressions for total energy in semiempirical MO theory, two cancellations between energy terms have been noted [16, 17]. It is

Table 1. *Energy values* (a.u.) *from selected SCF calculations*

	$-E_T$	$-1/2 \sum_i N(i)\varepsilon_i$	$-1/2 \sum_i N(i)E_i$	V_{NN}	V_{ee}	Δ	Δ'
HCl[a]	459.1468	140.9510	325.2535	7.0577	184.3025	−0.609	−0.423
H_2S[b]	397.8415	122.320	288.549	13.0276	166.229	−0.477	−0.222
PH_3[c]	341.3094	105.1020	253.7677	17.5603	148.6657	0.074	0.431
SiH_4[b]	290.5197	89.162	222.697	21.3393	133.535	−0.214	0.271
HF[d]	99.4785	29.1106	75.5612	5.1933	46.4506	0.098	0.243
H_2O[e]	75.6952	23.2142	61.6490	9.1680	38.4348	0.020	0.202
NH_3[f]	56.0052	18.1553	49.7833	11.9334	31.6280	0.057	0.354
CH_4[f]	40.1141	13.8288	39.6771	13.3918	25.8483	0.068	0.632
PN[g]	393.8211	121.7397	309.3419	37.2605	187.6022	0.606	1.242
P_2[c]	679.1664	208.5647	533.4509	62.8492	324.8862	0.460	1.035

[a] Present calculation.
[b] Ref. [3].
[c] Ref. [1].
[d] Ref. [18], Slater LCAO-MO's.
[e] Ref. [4].
[f] Ref. [19].
[g] Ref. [2].

worthwhile to examine at this point the energies of HCl and some other molecules for which comparable wave functions have been reported [1–4, 18, 19] because neither of the cancellations has been tested on second-row compounds before. The first cancellation [16] involves the core integrals (one-electron kinetic plus nuclear attraction energies) of the molecule (E_i) and separated atoms (E_i^a):

$$1/2 \sum_i N(i) E_i + V_{NN} - 1/2 \sum_a \sum_i N(i) E_i^a \equiv \Delta \approx 0 . \tag{1}$$

Here the first term is a sum (over all orbitals of occupation number $N(i)$) of the E_i from a molecular SCF calculation, V_{NN} is the nuclear repulsion energy in the molecule, and the last term involves summing over all orbitals on all constituent atoms the E_i^a from SCF calculations on the ground state atoms. In Hartree-Fock theory the total energy of a closed-shell molecule is given by any of the expressions,

$$E_T = \sum_i N(i) E_i + V_{ee} + V_{NN} = \sum_i N(i) \varepsilon_i - V_{ee} + V_{NN}$$
$$= 1/2 \sum_i N(i) \varepsilon_i + 1/2 \sum_i N(i) E_i + V_{NN} , \tag{2}$$

where V_{ee} is the interelectronic repulsion energy, and ε_i is the eigenvalue of the ith MO. Owing to the above cancellation [16], an approximation for the total energy for use in semiempirical MO methods where only eigenvalues are evaluated is

$$E_T \approx 1/2 \sum_{valence} N(i) \varepsilon_i + 1/2 \sum_{inner} N(i) \varepsilon_i + 1/2 \sum_a \sum_i N(i) E_i^a \tag{3}$$

and the atomization energy (neglecting relativistic and correlation energies) may similarly be crudely taken as

$$A \approx 1/2 \sum_i N(i) \varepsilon_i - \sum_a \sum_i N(i) \varepsilon_i^a . \tag{4}$$

Here the summing of the molecular eigenvalues, ε_i, is broken into a term for the MO's occupied by valence electrons and a term for the MO's occupied by the inner or core electrons. Such a differentiation allows the second term of (3) to be replaced by the eigenvalues from atomic SCF calculations, ε_i^a, in valence electron MO methods [20]. The atomic quantities needed in Eqs. (3) and (4) have been used extensively [2, 4, 20–22], and a tabulation for all first- and second-row elements based on both Slater atom and best atom exponents [15] appears in the Appendix. Returning to the examination of the cancellation of (1), we see in Table 1 that the value of Δ is large enough so that only the total energy may be reasonably approximated, and the atomization energy derived from (4) would appear to be of little value, except for comparative, order-of-magnitude purposes.

The second cancellation mentioned at the beginning of the preceding paragraph can be expressed as

$$- V_{ee} + V_{NN} + \sum_a V_{ee}^a \equiv \Delta' , \tag{5}$$

where V_{ee}^a is the interelectronic repulsion energy in each constituent atom of the molecule, and Δ' is about as small as the atomization energy [17]. Using the Slater atom data from the Appendix and from [15], Δ' is calculated (Table 1) to be on the average slightly larger than Δ.

Judging from the sizes of Δ and Δ' in Table 1 and elsewhere [4, 16, 17], it may be concluded that cancellations (1) and (5) hold better for first-row compounds than for second-row. The magnitude and sign of Δ and Δ' depend on whether one uses the Slater atom data from the Appendix (as we have done in Table 1) or the best atom data, but in either case the same picture of cancellations (1) and (5) emerges. Finally, it should be recognized that the main utility of (3) is as an alternative to taking $E_T = \sum_i N(i)\varepsilon_i$ in approximate MO methods where only the eigenvalues are directly assessible because some or most of the integrals in (2) are not evaluated.

A list of the unique, nonzero ($|F_{ij}| \geqq 0.0001$ a.u.) SCF Hamiltonian matrix elements of HCl is given in Table 2. The transferability of the matrix elements

Table 2. *Hamiltonian matrix elements* (a.u.) *of* HCl

	H $1s$	Cl $1s$	$2s$	$2p_\sigma$	$3s$	$3p_\sigma$	$3d_\sigma$
H $1s$	−0.5623						
Cl $1s$	−0.9391	−104.7410					
$2s$	−1.0467	− 31.7952	−19.0729				
$2p_\sigma$	−0.2634	− 0.0058	− 0.0152	−7.7892			
$3s$	−0.7839	− 1.2810	− 3.6814	−0.0130	−2.0546		
$3p_\sigma$	−0.5548	+ 0.0001	− 0.0079	−1.9078	−0.0427	−0.8732	
$3d_\sigma$	−0.2026	− 0.0005	− 0.0049	−0.0006	−0.0746	−0.2009	+0.5705

	Cl $2p_x$	Cl $3p_x$	Cl $3d_{xz}$
Cl $2p_x$	−7.7888		
$3p_x$	−1.8877	− 0.8568	
$3d_{xz}$	−0.0020	− 0.0278	+ 0.6941

can be employed to construct approximate wave functions for chemically related, large molecules. It is noted that the diagonal matrix elements for the $3d$ orbitals are positive and are of larger magnitude than the analogous matrix elements for compounds of Si, P, and S [1, 3].

Discussion of Computed Properties

Because wave functions of near Hartree-Fock quality have been obtained for HCl, the present wave function (which is easily generated by the usual computational techniques from the data in Table 2) is useful for appraising the near-minimum basis set wave functions which have been obtained for various compounds [1–3]. Hence a few one-electron properties were computed from the present wave function in order to see how close they are to those computed from better wave functions. For instance, the dipole moment (H^+Cl^-) of 0.82 D can be compared to the range of previously calculated values of $1.197 - 2.16$ and to the experimental value of 1.12 [11, 12]. The quadrupole moment of 3.003×10^{-26} esu cm^2 measured from the center of mass is smaller than other calculated values [11, 12] in the range $3.74 - 4.20 \times 10^{-26}$. The vertical ionization potential via Koopman's theorem of 11.29 eV is somewhat lower than the correspondingly calculated values of 12.94–13.50 and the experimental value of 12.74 [11, 12]. The dissociation energy of 3.35 eV with respect to the best atom energies [15] may be compared to calculated values in the range 3.37–3.76 eV and to the experimental value of 4.616 [11, 12].

A Mulliken population analysis gives a net atomic charge on Cl of -0.218. The H–Cl overlap population of 0.656 contains a contribution of only 0.067 from the Cl $3d_{z^2}$–H $1s$ interaction. The H–Cl overlap population follows a trend noted elsewhere [10] that the A–H overlap population decreases in the series SiH$_4$, PH$_3$, H$_2$S, HCl. The largest coefficients of the $3d$ orbitals are 0.098 for the $3d_\sigma$ AO in the 5σ MO and 0.025 for the $3d_\pi$ AO in the 2π MO. Consequently, the $3d$ orbitals in HCl may be described as polarization functions [5, 23]. This character of the $3d$ orbitals might also be inferred from the fairly small (0.055) occupation of the $3d_\sigma$ AO and very small (0.001) occupation of each $3d_\pi$ AO. When more functions are added to the basis set of HCl, thereby causing the basis functions to lose some of their chemical interpretability, the coefficients of the $3d$ functions are known to become even smaller. The monotonically decreasing $3d$ orbital populations [1, 3] in the SiH$_4$ to HCl series seem to reflect the ability of the $3d$ functions to describe the electron density in the A–H bonding regions. It is significant that the trends in the A–H overlap populations and in the $3d$ orbital occupations as found from the near-minimum Slater-type orbital basis sets [1, 3, 10] are also obtained with Gaussian-type orbitals [11].

In Fig. 1 various electron density contour maps of HCl are presented. The charge distributions are computed according to the description given elsewhere [10], and the reference atomic densities for the difference maps are calculated from the best atom wave function [15] of Cl and the $1s$ Slater-type orbital (exponent 1.2) for H. The first feature to be noted is the qualitative similarity of the total, difference, and orbital maps to analogous ones computed from near Hartree-Fock wave functions [24]. Hence useful information may be obtained from these near-

minimum basis set densities [10]. The difference maps (molecular minus atomic densities) depend drastically on whether they are computed with respect to spherically or cylindrically averaged reference atomic densities (Fig. 1b *vs.* 1c). The use of spherically symmetric atomic densities appears to be more appropriate because of reasons given before [10] and because the atomic wave functions usually employed are computed [25] subject to spherical symmetry restrictions [26]. By separating [10] the density due to "core" electrons from the density due to the "valence" electrons, it is seen in Fig. 1h that the "core" electron density is largely unpolarized as expected, although there is a small displacement of electrons toward the internuclear region. This displacement is interpreted as meaning the low-lying MO's of HCl possess some slight bonding character. Also, the similarity of the "valence" electron difference map (Fig. 1i) to the difference map computed with all electrons (Fig. 1b) means that the "valence" electrons are responsible for the gross redistributions of charge which occur upon molecular formation.
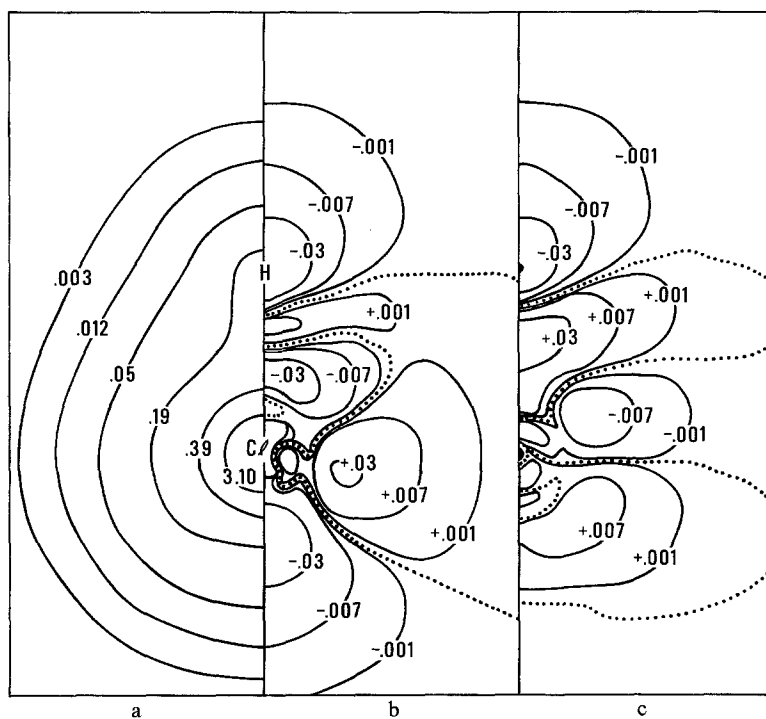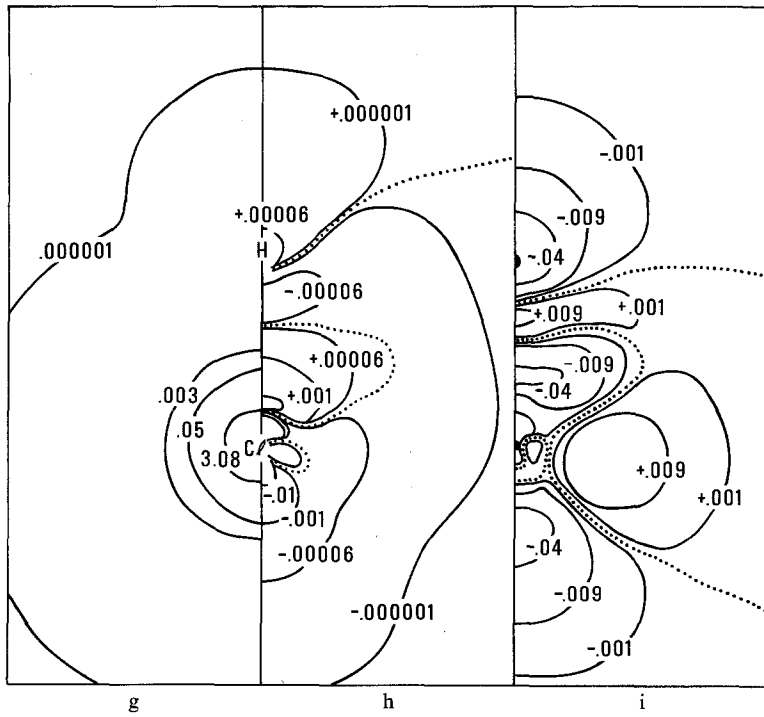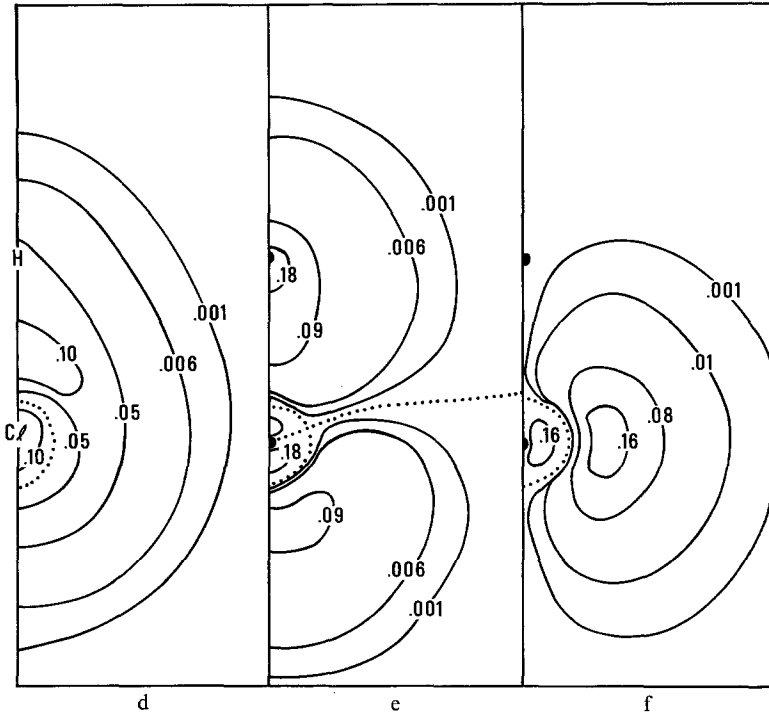

Fig. 1a–i. Electron density maps of HCl. Contours are in atomic units, with nodes denoted by dotted lines. The area covered by each map is 1.8 × 4.8 Å. Density at the Cl and H nuclei, respectively, in the individual maps are: a total density, 3179.15, 0.39; b difference density computed with a spherical atomic Cl distribution, −0.94, −0.18; c difference density computed with a cylindrical, valence state ($3p_\sigma$ AO singly occupied) atomic Cl distribution, −0.94, −0.18; d density of doubly occupied 4σ MO, 24.32, 0.09; e density of doubly occupied 5σ MO, 2.95, 0.30; f density of doubly occupied $2\pi_x$ MO, zero at nuclei; g core density from 1σ, 2σ, 3σ, and 1π MO's, 3151.88, 0.0003; h difference density computed from core density minus density of the SCF Cl 1s, 2s, and 2p AO's, +0.25, +0.0002; i difference density computed from valence density (4σ, 5σ, 2π MO's) minus density of atomic H 1s and spherically averaged SCF Cl 3s and 3p AO's, −1.19, −0.18

.001
.006
.18
.09

.001
.01
.08
.16
.16

H
.001
.10
.006
.05
Cℓ
.10
.05

.18
.09

.06
.001

d   e   f

+.000001
-.001
-.009
+.00006
-.04
H
-.00006
+.009   +.001
+.00006
-.009
.000001
+.001
-.04
.003
.05
3.08 Cℓ
-.01
-.001
+.009
+.001
-.00006
-.04
-.009
-.000001
-.001

g   h   i

Appendix: Atomic SCF Eigenvalues and Core Integrals

All quantities are in atomic units (1 a.u. = 27.2098 eV); valence orbitals are 1s for H–He, 2s, p for Li–Ne, and 3s, p for Na–Ar; and exponent for H 1s is 1.0 in columns 1–3; 1.2 in columns 4–6

	Slater exponents			Best atom exponents		
	$-\frac{1}{2}\sum_{inner} N(i)\,\varepsilon_i^a$	$-\frac{1}{2}\sum_{valence} N(i)\,\varepsilon_i^a$	$-\frac{1}{2}\sum_{all} N(i)\,E_i^a$	$-\frac{1}{2}\sum_{inner} N(i)\,\varepsilon_i^a$	$-\frac{1}{2}\sum_{valence} N(i)\,\varepsilon_i^a$	$-\frac{1}{2}\sum_{all} N(i)\,E_i^a$
H	—	0.2500	0.2500	—	0.2400	0.2400
He	—	0.8925	1.9550	—	0.8965	1.9512
Li	2.4527	0.0973	4.8683	2.4602	0.0974	4.8608
Be	4.6949	0.3049	9.5562	4.7171	0.3087	9.5310
B	7.6182	0.6136	16.2632	7.6778	0.6341	16.1865
C	11.2240	1.0409	25.3537	11.3016	1.0791	25.2417
N	15.5126	1.5960	37.1566	15.5938	1.6476	37.0275
O	20.4838	2.0481	52.0010	20.6140	2.1575	51.7688
F	26.1378	2.5779	70.2160	26.3029	2.7467	69.8926
Ne	32.4746	3.1944	92.1305	32.6622	3.4178	91.7322
Na	46.4595	0.0858	114.5427	46.7642	0.0876	114.2722
Mg	58.5205	0.2498	139.9962	58.6308	0.2410	139.9861
Al	72.2427	0.4912	168.2413	71.9440	0.4340	168.7758
Si	86.8511	0.8264	200.1442	86.6443	0.7621	200.6836
P	102.7246	1.2705	235.5310	102.6158	1.1811	236.1130
S	119.8754	1.6897	274.5446	119.9639	1.5860	275.0778
Cl	138.3056	2.2085	317.3365	138.5813	2.0865	317.8560
Ar	157.9949	2.8342	364.0877	158.4696	2.6937	364.6020

References

1. Boyd, D. B., Lipscomb, W. N.: J. chem. Physics **46**, 910 (1967).
2. — — J. chem. Physics **48**, 4968 (1968).
3. Boer, F. P., Lipscomb, W. N.: J. chem. Physics **50**, 989 (1969).
4. Boyd, D. B., Lipscomb, W. N.: J. chem. Physics **48**, 4955 (1968); Newton, M. D., Boer, F. P., Lipscomb, W. N.: J. Amer. chem. Soc. **88**, 2353, 2367 (1966).
5. Coulson, C. A.: Nature **221**, 1106 (1969).
6. Mitchell, K. A. R.: Chem. Reviews **69**, 157 (1969).
7. Webster, B. C.: J. chem. Soc. (London) A **1968**, 2909.
8. Hillier, I. H., Saunders, V. R.: Int. J. quant. Chemistry **4**, 203 (1970); — —: J. chem. Soc. (London) A **1970**, 2475; Marsmann, H., Groenweghe, L. C. D., Schaad, L. J., Van Wazer, J. R.: J. Amer. chem. Soc. **92**, 6107 (1970).
9. Shatenshtein, A. I., Gvozdeva, H. A.: Tetrahedron **25**, 2749 (1969); Urch, D. S.: J. chem. Soc. (London) A, **1969**, 3026; Cowley, A. H., Dewar, M. J. S., Jackson, W. R., Jennings, W. B.: J. Amer. chem. Soc. **92**, 5206 (1970); Boyd, D. B.: Theoret. chim. Acta (Berl.) **18**, 184 (1970); Boyd, D. B., Hoffmann, R.: J. Amer. chem. Soc., in press.
10. Boyd, D. B.: J. chem. Physics **52**, 4846 (1970).
11. Rothenberg, S., Young, R. H., Schaefer, H. F.: J. Amer. chem. Soc. **92**, 3243 (1970).
12. Moccia, R.: J. chem. Physics **37**, 910 (1962); Nesbet, R. K.: J. chem. Physics **41**, 100 (1964); Scrocco, E., Tomasi, J.: Molecular orbitals in chemistry, physics and biology, p. 263. New York: Academic Press 1964; Banyard, K. E., Hake, R. B.: J. chem. Physics **44**, 3523 (1966); Cade, P. E., Huo, W. M.: J. chem. Physics **45**, 1063 (1966); **47**, 649 (1967); McLean, A. D., Yoshimine, M.: J. chem. Physics **47**, 3256 (1967); Moccia, R.: Theoret. chim. Acta (Berl.) **8**, 8 (1967).
13. Wahl, A. C., Bertoncini, P. J.: Argonne National Laboratory Report 7271 (1967); Wahl, A. C., Bertoncini, P., Kaiser, K., Land, R.: Int. J. quant. Chemistry **3 S**, 499 (1970).
14. Herzberg, G.: Spectra of diatomic molecules. Princeton, N. J.: D. Van Nostrand Co. 1950.
15. Clementi, E., Raimondi, D. L.: J. chem. Physics **38**, 2686 (1963).
16. Boer, F. P., Newton, M. D., Lipscomb, W. N.: Proc. nat. Acad. Sci. USA **52**, 890 (1964).
17. Goodisman, J.: J. Amer. chem. Soc. **91**, 6552 (1969).
18. Ransil, B. J.: Rev. mod. Physics **32**, 245 (1960).
19. Palke, W. E., Lipscomb, W. N.: J. Amer. chem. Soc. **88**, 2384 (1966).
20. Boyd, D. B., Lipscomb, W. N.: J. theoret. Biol. **25**, 403 (1969).
21. Boer, F. P., Shannon, T. W., McLafferty, F. W.: J. Amer. chem. Soc. **90**, 7239 (1968).
22. Boyd, D. B.: Theoret. chim. Acta (Berl.) **14**, 402 (1969).
23. Lehn, J. M., Munsch, B.: J. chem. Soc. (London) D **1969**, 1327.
24. Cade, P. E., Bader, R. F. W., Henneker, W. H., Keaveny, I.: J. chem. Physics **50**, 5313 (1969).
25. Roothaan, C. C. J., Bagus, P. S.: Methods in computational physics, Vol. 2, p. 47. New York: Academic Press 1963.
26. — Rev. mod. Physics **32**, 179 (1960).

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