

# Self-Consistent-Field Wave Functions of P<sub>2</sub> and PO, and the Role of d Functions in Chemical Bonding and of s-p Hybridization in N<sub>2</sub> and P<sub>2</sub>

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**Abstract:** The results of accurate SCF calculations on P<sub>2</sub> and PO are reported. At the equilibrium distance  $R_e$ , the d population is about 0.34 electron for the two P atoms in P<sub>2</sub>, 0.29 electron for the P atom in PO, and 0.05 electron for the O atom; this d participation approximately confirms the results of Boyd and Lipscomb. As  $R$  decreases, d participation in P<sub>2</sub> increases markedly. At  $R_e$ , deletion of d and f functions from the basis set increases the computed energy by 0.093 au (2.53 eV) in P<sub>2</sub> and 0.114 au (3.10 eV) in PO. Comparisons with Cl<sub>2</sub> and N<sub>2</sub> are discussed; d and f participation is smaller, but in N<sub>2</sub> its energetic effect is about the same (0.095 au or 2.58 eV) as in P<sub>2</sub>; in Cl<sub>2</sub> the energy effect is somewhat smaller (0.059 au or 1.61 eV). It is argued that d participation in second-row atoms, and even in first-row atoms, when they enter molecules, can properly be thought of as a chemical effect. The contribution of free isovalent s-p hybridization to bonding in N<sub>2</sub> and P<sub>2</sub> is explored by deleting valence-shell p functions from the LCAO functions used by the valence-shell  $\sigma_u$  MO in these molecules. By these deletions the energy is increased by 0.12 au (3.3 eV) in N<sub>2</sub> but only by 0.02 au (0.5 eV) in P<sub>2</sub>; this difference helps to explain the difference in properties of N<sub>2</sub> and P<sub>2</sub>. Some additional probable free hybridization in the  $\sigma_g$  MO's is also discussed. In F<sub>2</sub> the energy effect of d participation is about half as large as in Cl<sub>2</sub>.

The role of d orbitals—better, d functions—in bonding in the compounds of second-row atoms has been extensively discussed.<sup>3–20</sup> As is well known, it is necessary in LCAO expressions, even for first-row-atom compounds, to include d functions if one wishes

to obtain reasonably accurate expressions for SCF MO's. These d functions, which are *shrunk* as compared with free-atom d orbitals (present only in excited states), are needed for "valence polarization" of the free-atom s and p orbitals.<sup>21</sup> For second-row-atom compounds, d function participation is increased. In transition metal compounds, s, p, and d functions are all of comparable importance, and one speaks of "hybridization" and "chemical" participation: here the d functions are not especially shrunk as compared with d orbitals of the free atoms. Much has been written about the size of d orbitals in various states of atoms and their ions (*cf.* ref 3 for a review); when free-atom d orbitals are large, the energy cost of shrinking them to required size for molecular LCAO use is large, and this use is disfavored. On the other hand, if an atom in a molecule acquires a considerable positive charge, as for example notably the S atom in SF<sub>6</sub>, d function utilization is strongly favored and the d function LCAO coefficients become relatively large.

In evaluating the importance of d functions for LCAO-MO's, it is important to start with an ample basis set of s and p STF's (Slater-type functions). If a d function is added to a minimal s, p basis set, one obtains a much exaggerated d participation as compared with that for d addition to a full s, p set. This is because linear combinations of d functions on different atoms are in general not independent of similar linear combinations of s or p functions, and so can in part take the place of the latter. Here one should note that a reasonably accurate expression for the AO of a free atom requires several s and p STF's. Not unless these have been used in the LCAO expression for an MO should d participation be counted. As an example, Lipscomb, *et al.*,<sup>7</sup> using a minimal s, p set plus a d orbital obtain d orbital populations of 0.447, 0.290,

(21) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962), Section II.2.

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(2) (a) Assisted in part by Contract No. N00014-67-A-0285-0001 with the University of Chicago; (b) assisted in part by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission, and the Florida State University.

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**Table I.** Basis Set of STF's with  $\zeta$  Values in Parentheses, for  $P_2$ , Followed by  $\epsilon$  Values and LCAO Coefficients of MO's for  $R = 3.4974$  au<sup>a</sup>

	(a) $\sigma$ STF's									
	$-\epsilon$	$1\sigma_g$ 79.968	$1\sigma_u$ 79.968	$2\sigma_g$ 7.512	$2\sigma_u$ 7.511	$3\sigma_g$ 5.405	$3\sigma_u$ 5.402	$4\sigma_g$ 0.911	$4\sigma_u$ 0.602	$5\sigma_g$ 0.409
1s (15.9516)		0.595	0.595	-0.147	-0.148	0.000	-0.000	0.040	0.038	-0.008
1s (23.000)		0.018	0.018	-0.013	-0.013	0.000	-0.000	0.003	0.004	-0.002
2s (5.5936)		0.005	0.005	0.669	0.670	-0.001	-0.000	-0.198	-0.193	0.047
2s (14.5107)		0.111	0.111	-0.104	-0.104	0.000	-0.000	0.027	0.029	-0.010
3s (2.4295)		0.001	0.001	0.002	0.002	0.001	-0.000	0.363	0.390	-0.119
3s (1.5022)		-0.001	-0.002	0.000	0.003	-0.001	-0.003	0.271	0.372	-0.199
3s (4.7000)		-0.002	-0.002	0.114	0.115	-0.000	-0.000	-0.091	-0.082	0.009
3s (0.9000)			-0.001		0.004	0.000	-0.005	-0.010	-0.059	-0.063
2p $\sigma$ (6.5053)						0.467	0.467	-0.049	0.045	-0.122
2p $\sigma$ (12.5000)						0.025	0.026	-0.003	0.002	-0.006
3p $\sigma$ (2.0351)						0.007	0.006	0.132	-0.150	0.402
3p $\sigma$ (1.1978)			-0.002		0.003	-0.001	-0.005	0.041	-0.134	0.275
3p $\sigma$ (4.8605)						0.267	0.267	-0.032	0.028	-0.077
3p $\sigma$ (0.7200)					0.001	0.001	-0.001	-0.012	-0.013	-0.032
3d $\sigma$ (3.1400)				-0.001	-0.001	0.000	0.000	0.008	-0.003	0.010
3d $\sigma$ (1.5580)				0.001	0.001	0.001	-0.001	0.054	-0.013	0.060
3d $\sigma$ (0.9280)						0.001	-0.001	-0.008	-0.007	-0.027
4f $\sigma$ (2.8410)						-0.000	-0.000	0.004	-0.000	0.004
4f $\sigma$ (1.5480)						0.001	0.000	0.009	-0.001	0.002

  

	(b) $\pi$ STF's							
	$-\epsilon$	$1\pi_u$ 5.403	$1\pi_g$ 5.403	$2\pi_u$ 0.377	$-\epsilon$	$1\pi_u$ 5.403	$1\pi_g$ 5.403	$2\pi_u$ 0.377
		Coefficients				Coefficients		
2p $\pi$ (6.5053)		0.466	0.466	-0.104	3d $\pi$ (3.1400)	-0.000	-0.000	0.009
2p $\pi$ (12.5000)		0.026	0.026	-0.006	3d $\pi$ (1.5580)	-0.000	-0.000	0.073
3p $\pi$ (2.0351)		0.007	0.007	0.329	3d $\pi$ (0.9280)	0.000	0.001	0.015
3p $\pi$ (1.1978)		-0.002	-0.002	0.301	4f $\pi$ (2.841)	-0.000	-0.000	0.004
3p $\pi$ (4.8605)		0.268	0.268	-0.065	4f $\pi$ (1.5480)	0.000	0.000	0.014
3p $\pi$ (0.7200)		0.001	0.002	0.008				

<sup>a</sup> For  $\sigma_u$  MO's, the sign refers to one atom; for the other atom, the sign is reversed.

and 0.147 in LCAO-MO computations on  $SiH_4$ ,  $PH_3$ , and  $H_2S$ , while Rothenberg, *et al.*,<sup>16</sup> using a full s, p basis set, obtain the respective d populations 0.108, 0.082, and 0.063.

Boyd and Lipscomb<sup>7a</sup> have made LCAO-SCF calculations on  $P_2$  and PO (also  $PH_3$  and  $PO^-$ ) using a minimal s, p set plus one  $3d\sigma$  and one  $3d\pi$  STF. It seemed desirable to repeat these calculations using a full basis set of s and p functions, plus added d and f functions, and this has been done here. The effects of omitting the d and f functions (for either or both atoms in the case of PO) were also explored. Further, the effect of deleting p functions, hence deleting s-p hybridization, in the valence-shell  $\sigma_u$  MO of  $P_2$  and of  $N_2$  was examined, since in an earlier paper<sup>22</sup> it was concluded that the strong bonding observed in  $N_2$  would largely disappear if it were not for this hybridization.

### Calculations and Results

In the calculations on  $P_2$  and PO, the s, p basis set for the P atom was taken from Clementi's "Tables of Atomic Functions,"<sup>23</sup> supplemented, however, by adding a  $3s$  (0.90), a  $3p\sigma$  (0.72), and a  $3p\pi$  (0.72) STF (the numbers in parentheses are orbital exponents). To these (see Table I), the d and f functions shown in Table I were added. Similar choices were made for the O atom in PO (see Table V). With these basis sets, the results obtained should be close to accurate

(22) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

(23) Available on request as a supplement to E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

SCF-MO ("Hartree-Fock") values. The calculations were carried out with the 360-91 computer at the IBM Research Laboratory in San Jose, Calif., using the ALCHEMY computer program written by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine of the theoretical chemistry group there.<sup>24</sup>

For  $P_2$ , calculations were made at several internuclear distances  $R$  as follows: 3.28, 3.51, 3.58 (the experimental equilibrium distance  $R_e$ ), 3.70, and 3.88 au. From the resulting computed energy values, the SCF computed  $R_e$  was determined as 3.4974 au. The corresponding spectroscopic constants are  $\omega_e = 919.73$ ,  $x_e\omega_e = 3.88$ ,  $B_e = 0.3179$ ,  $\alpha_e = 0.00102$   $cm^{-1}$ . The respective experimental values are 780.4, 2.804, 0.3033, and 0.00142.

For  $P_2$  the ground-state electron configuration is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^4$ . The basis set of STF's and LCAO coefficients and the orbital energies  $\epsilon$  of the MO's at  $R = 3.4974$  au are listed in Table I. The manner in which the coefficients of the d and f STF's vary with  $R$  is shown in Table II (the minor variation of the other coefficients with  $R$  is of no great interest). Table III shows the computed total energy for a range of  $R$  values, both using the full basis set and with the d and f functions deleted from the set and the SCF computation carried

(24) A preliminary description of the program is given by A. D. McLean, "Current and Projected Capabilities of the ALCHEMY Computer Program," in the Proceedings of the Conference on Potential Surfaces in Chemistry, held at the University of California, Santa Cruz, Calif., Aug 1970. This is available from the IBM Research Laboratory in San Jose.

**Table II.** Variation of d and f STF Coefficients with  $R$  for Valence-Shell MO's of  $P_2^a$ 

	$4\sigma_g$		$4\sigma_u$		$5\sigma_g$		$1\pi_g$	
	3.28	3.88	3.28	3.88	3.28	3.88	3.28	3.88
$3d\sigma$ (3.140)	0.011	0.004	-0.003	-0.002	-0.012	-0.007		
$3d\sigma$ (1.558)	0.060	0.042	-0.014	-0.012	-0.062	-0.055		
$3d\sigma$ (0.928)	-0.016	0.000	-0.006	-0.009	0.040	0.011		
$4f\sigma$ (2.841)	0.005	0.002	-0.000	-0.000	-0.006	-0.002		
$4f\sigma$ (1.548)	0.007	0.010	-0.000	-0.002	0.001	-0.006		
$3d\pi$ (3.140)							0.012	0.006
$3d\pi$ (1.558)							0.083	0.056
$3d\pi$ (0.928)							0.010	0.021
$4f\pi$ (2.841)							0.006	0.002
$4f\pi$ (1.548)							0.014	0.014

<sup>a</sup> For the inner-shell MO's, the coefficients are very small (0.00013 for  $d\pi$  and 0.00026 for  $f\pi$  in  $1\pi_u$  and  $1\pi_g$ ).

**Table III.** Total Energy (au) with Full Basis Set and  $E_{df}$  with d and f Functions Deleted, for  $P_2$ 

$R$ , au	$-E$	$-E_{df}$	$\Delta E_{df}$
3.28	681.48682	681.37668	0.11014
3.4978	681.50039	681.40743	0.09296
3.58	681.49880	681.41183	0.08697
3.70	681.49172	681.41296	0.07876
3.88	681.47331	681.40582	0.06749

in those tables. During the experimentation mentioned, the calculated populations on the P and O atoms varied considerably. This fact, together with the occurrence of appreciable negative computed d populations in some of the AO's for some of the MO's (see Table VII), indicates that the usual population analysis<sup>25</sup> is of somewhat limited significance, perhaps especially with large basis sets.<sup>27</sup> For example, O atom populations varying from 8.62 to 8.58 were obtained with certain

**Table IV.** Atomic Orbital Populations of Valence-Shell MO's in  $P_2^{a,b}$ 

MO	$R = 3.28$ au				$R = 3.4974$ au			
	s	p	d	f	s	p	d	f
$4\sigma_g$	1.67 (1.65)	0.28 (0.35)	0.046	0.004	1.70 (1.69)	0.25 (0.31)	0.046	0.005
$5\sigma_g$	0.40 (0.50)	1.56 (1.50)	0.041	0.001	0.34 (0.43)	1.63 (1.57)	0.033	0.000
Sums	2.07 (2.15)	1.84 (1.85)			2.04 (2.12)	1.88 (1.88)		
$4\sigma_u$	1.39 (1.75)	0.59 (0.25)	0.019	0.000	1.47 (1.78) <sup>c</sup>	0.51 (0.22) <sup>c</sup>	0.019	0.001
$2\pi_u$		3.69 (4.00)	0.273	0.033	2.04 (2.12)	3.73 (4.00)	0.240	0.032
Total $\sigma$			0.105	0.005			0.099	0.006
Total			0.379	0.039			0.339	0.037

<sup>a</sup> The figures in parentheses refer to calculations in which the d and f functions were deleted. <sup>b</sup> For the inner-shell MO's  $1\sigma_g$ ,  $1\sigma_u$ ,  $2\sigma_g$ ,  $2\sigma_u$ ,  $3\sigma_g$ ,  $3\sigma_u$ ,  $1\pi_u$ , and  $1\pi_g$ , the d populations were 0.0003 or less and the f populations 0.0002 or less. The s populations were within 0.001 or less of 2.000 for  $1\sigma_g$ ,  $1\sigma_u$ ,  $2\sigma_g$ , and  $2\sigma_u$ , and the p populations were within 0.0007 of 2.000 for  $3\sigma_g$  and  $3\sigma_u$  and within 0.0002 of 4.0000 for  $1\pi_u$  and  $1\pi_g$ . <sup>c</sup> The shift in population from p toward s in the  $4\sigma_u$  MO on deleting the d and f functions reflects changes in the LCAO coefficients in Table I, of which the most important are as follows: for 3s (2.4295), 3s (1.5022), and 3s (0.90) the respective coefficients change from 0.390, 0.372, and -0.059 to 0.410, 0.464, and 0.022, while for 3p $\sigma$  (2.0351) and 3p $\sigma$  (1.1978) they change from -0.150 and -0.134 to -0.125 and -0.029. For the  $4\sigma_g$  and  $5\sigma_g$  MO's, the changes in s and p LCAO coefficients and populations are much smaller.

out with the diminished basis set. Table IV shows the populations<sup>25</sup> of the s, p, d, and f STF's in the valence-shell MO's at two values of  $R$ , both when the full basis set is used and when the d and f STF's are deleted. Tables II, III, and IV show that the participation of the d STF's in bonding increases considerably with decreasing  $R$ . Table IV also shows that the deletion of the d and f STF's causes, in the case of the  $4\sigma_u$  MO only, a considerable shift from p toward s coefficients (footnote c) and populations.

For PO (electron configuration  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi$ ) calculations were made only for  $R = 2.738$  au, approximately the experimental  $R_e$  value.<sup>26</sup> After some experimentation with the d STF's used, the basis set given in Table V was adopted, with resulting  $\epsilon$  values and LCAO coefficients as given

(25) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(26) This corresponds to the  $R_e$  value (1.447 Å) given by G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950. More recent values are 1.473 and 1.475 Å: K. S. Rao, *Can. J. Phys.*, **36**, 1526 (1958); N. L. Singh, *ibid.*, **37**, 136 (1959).

choices, but when the STF  $3d\sigma_O$  (1.30) included in the finally chosen basis set was then added, the computed O atom population dropped to the value 8.45 indicated in Table VI. Table VI shows the computed total energy for the full basis set and for basis sets with deletions of d and f STF's of one or both atoms. It shows also the corresponding computed charges on the two atoms (e.g.,  $-Q_O =$  total computed O atom population minus 8). These charges are seen to be very sensitive to the presence or absence of d and f STF's in the basis set. Table VII gives a detailed survey of the STF populations for wave functions based on the full basis set, and on this set with various deletions.

Table VIII is concerned with a comparison between  $N_2$  and  $P_2$  with respect to the effect on the total energy of deleting d and f functions from the basis set, and also (see footnote b) of deleting valence-shell p $\sigma$  functions from the valence-shell  $\sigma_u$  MO, a deletion whose effect is to remove practically all s-p hybridization (see

(27) Cf. C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964).

Table V. Basis Set of STF's with  $\zeta$  Values in Parentheses, Followed by  $\epsilon$  Values and LCAO Coefficients<sup>a</sup> of MO's for PO with  $R = 2.738$  au

	(a) $\sigma$ STF's								
	$-\epsilon$	$1\sigma$ 80.0230	$2\sigma$ 20.5806	$3\sigma$ 7.5615	$4\sigma$ 5.4530	$5\sigma$ 1.3607	$6\sigma$ 0.7341	$7\sigma$ 0.5403	
1s <sub>P</sub> (15.9516)		0.842	0.000	-0.209	0.000 (0.002)	0.021 (0.026)	0.045 (0.049)	-0.024 (-0.016)	
1s <sub>P</sub> (23.0000)		0.025		-0.019	0.000 (0.001)	0.002 (-0.000)	0.005 (0.004)	-0.003 (-0.006)	
2s <sub>P</sub> (5.5936)		0.007		0.947	-0.003 (-0.014)	-0.109 (-0.110)	-0.226 (-0.229)	0.118 (0.111)	
2s <sub>P</sub> (14.5107)		0.156		-0.147	0.000 (0.002)	0.016 (0.012)	0.036 (0.035)	-0.019 (-0.023)	
3s <sub>P</sub> (2.4295)		0.001		0.002 (0.003)	-0.001 (0.002)	0.178 (0.233)	0.473 (0.526)	-0.265 (-0.185)	
3s <sub>P</sub> (1.5022)		-0.004 (-0.001)		-0.003 (-0.001)	-0.009 (-0.001)	0.143 (0.017)	0.465 (0.449)	-0.307 (-0.440)	
3s <sub>P</sub> (4.7000)		-0.004 (-0.009)		0.161	-0.000	-0.043 (-0.067)	-0.090 (-0.105)	0.046 (0.014)	
3s <sub>P</sub> (0.9000)		-0.001 (0.000)		-0.001(0.000)	-0.002 (0.001)	-0.008 (0.014)	0.023 (0.024)	-0.010 (-0.029)	
2p <sub>σP</sub> (6.5053)				(0.006)	0.660 (0.659)	-0.061 (-0.062)	-0.006 (0.000)	-0.119 (-0.117)	
2p <sub>σP</sub> (12.5000)					0.036	-0.003	-0.000 (-0.001)	-0.006 (-0.007)	
3p <sub>σP</sub> (2.0351)				(0.001)	0.006 (0.010)	0.141 (0.171)	0.002 (0.024)	0.383 (0.431)	
3p <sub>σP</sub> (1.1978)		-0.002 (0.000)		-0.002 (-0.001)	-0.009 (-0.003)	0.043 (-0.081)	0.016 (-0.067)	0.226 (0.045)	
3p <sub>σP</sub> (4.8605)				0.001	0.378	-0.037 (-0.040)	-0.002 (-0.005)	-0.074 (-0.081)	
3p <sub>σP</sub> (0.7200)					0.001	0.000 (0.032)	0.011 (0.023)	-0.010 (0.027)	
3d <sub>σP</sub> (3.4800)				-0.001	0.001	0.011	0.005	0.014	
3d <sub>σP</sub> (1.7200)					-0.002	0.063	0.021	0.083	
3d <sub>σP</sub> (1.0300)		-0.001		-0.001	-0.001	-0.002	0.007	0.009	
4f <sub>σP</sub> (2.8410)					-0.001	0.009	0.005	0.009	
4f <sub>σP</sub> (1.5480)						0.008	0.005	0.004	
1s <sub>O</sub> (7.6063)			0.935		-0.001	-0.198 (-0.199)	0.084 (0.091)	0.014 (0.019)	
1s <sub>O</sub> (13.2240)			0.041			-0.005 (-0.002)	0.001 (0.002)	0.000 (0.003)	
2s <sub>O</sub> (3.1441)		0.001 (0.000)	0.004	0.001 (0.000)	0.002 (0.001)	0.405 (0.372)	-0.218 (-0.235)	-0.061 (-0.104)	
2s <sub>O</sub> (6.3783)			0.035			-0.092 (-0.079)	0.035 (0.040)	0.004 (0.022)	
2s <sub>O</sub> (1.8792)		-0.001 (-0.000)	-0.001	(0.001)	0.002 (0.004)	0.536 (0.609)	-0.242 (-0.248)	-0.028 (0.026)	
2s <sub>O</sub> (1.1200)		0.005 (0.001)	0.001	0.005 (-0.001)	0.013 (-0.003)	-0.117 (-0.058)	-0.253 (-0.238)	-0.207 (-0.097)	
2p <sub>σO</sub> (1.7960)		0.001 (0.040)	0.002	(-0.001)	-0.002 (-0.005)	-0.175 (-0.237)	-0.372 (-0.332)	-0.398 (-0.445)	
2p <sub>σO</sub> (3.4379)			-0.001 (-0.002)			-0.040 (-0.038)	-0.167 (0. -149)	-0.199 (-0.191)	
2p <sub>σO</sub> (1.1536)		-0.003 (-0.000)	-0.001	-0.003 (0.001)	-0.008 (0.003)	0.096 (0.071)	0.070 (0.072)	-0.019 (-0.062)	
2p <sub>σO</sub> (7.9070)			-0.001			-0.004 (-0.006)	-0.009 (-0.008)	-0.010 (-0.013)	
3d <sub>σO</sub> (1.3000)						-0.023	-0.021	-0.015	
3d <sub>σO</sub> (2.0000)			-0.001	0.001	0.004	0.036	0.026	0.032	
3d <sub>σO</sub> (3.0000)						0.002	0.006	0.005	
4f <sub>σO</sub> (2.6000)					-0.001	-0.007	-0.005	-0.008	
	(b) $\pi$ STF's								
	$-\epsilon$	$1\pi$ 5.4527	$2\pi$ 0.5485	$3\pi$ 0.3188		$-\epsilon$	$1\pi$ 5.4527	$2\pi$ 0.5485	$3\pi$ 0.3188
2p <sub>πP</sub> (6.5053)		0.659	-0.074 (-0.080)	0.140 (0.143)	4f <sub>πP</sub> (1.5480)			0.009	0.029
2p <sub>πP</sub> (12.5000)		0.036	-0.004 (-0.005)	0.007 (0.007)	2p <sub>πO</sub> (1.7960)			0.441 (0.445)	0.211 (0.165)
3p <sub>πP</sub> (2.0351)		0.010	0.240 (0.287)	-0.472 (-0.467)	2p <sub>πO</sub> (3.4379)			0.254 (0.246)	0.144 (0.188)
3p <sub>πP</sub> (1.1978)		-0.004 (-0.003)	0.123 (0.146)	-0.532 (-0.611)	2p <sub>πO</sub> (1.1536)		0.001 (-0.000)	0.190 (0.205)	0.158 (0.384)
3p <sub>πP</sub> (4.8605)		0.379	-0.048 (-0.058)	0.083 (0.080)	2p <sub>πO</sub> (7.9070)			0.013 (0.014)	0.006 (0.007)
3p <sub>πP</sub> (0.7200)		0.001	-0.011 (-0.024)	-0.040 (-0.045)	3d <sub>πO</sub> (2.000)		-0.001	-0.053	-0.012
3d <sub>πP</sub> (3.4800)		0.001	0.011	0.012	3d <sub>πO</sub> (3.0000)			0.001	0.005
3d <sub>πP</sub> (1.7200)		-0.001	0.082	0.078	4f <sub>πO</sub> (2.6000)			0.012	0.002
3d <sub>πP</sub> (1.0300)			0.000	0.136	3d <sub>πO</sub> (1.0000)			-0.001	0.015
4f <sub>πP</sub> (2.8410)			0.011	0.003					

<sup>a</sup> Coefficients in parentheses are for the case that the d and f functions are omitted. Where nothing is given in parentheses, the value is unchanged (or zero for d and f functions). For other blank spaces, the value is 0.000.

**Table VI.** Total Energy  $E$  (au) and Atomic Charges  $Q(e)$  with Full Basis Set and with Various Deletions, for PO, with  $R = 2.738$  au

	$-E$	$\Delta E$	$Q_P$	$Q_O$
Full basis set	415.6303		0.45	-0.45
Delete d and f for O	415.6140	0.0163	-0.12	0.12
Delete d and f for P	415.5936	0.0367	1.13	-1.13
Delete all d and f	415.5165	0.1139	0.66	-0.66
Delete only $3d\sigma_O(1.30)$	415.6302	0.0001	0.62	-0.62

greater than the  $d\sigma$  participation. Table II indicates that d participation in  $P_2$  increases with decreasing  $R$ , and presumably this is a general phenomenon.

Table X compares d populations in  $P_2$ , PO,  $Cl_2$ , and  $N_2$ . The  $d\sigma$  participation is almost as large in  $Cl_2$  as in  $P_2$  (0.09 as against 0.10), but the  $d\pi$  participation is very much less (0.07 as against 0.34). This difference can doubtless be attributed to much smaller  $\pi$  overlap in  $Cl_2$ , due to the larger  $R$  (relative to atomic

**Table VII.** Atomic Orbital Populations of Valence-Shell MO's for PO, with  $R = 2.738$  au<sup>a,b</sup>

MO	$s_P$	$p_P$	$d_P$	$f_P$	$s_O$	$p_O$	$d_O$	$f_O$
$5\sigma$	0.29 (0.21) (-0.03, 0.40)	0.18 (0.10) (-0.03, 0.28)	0.05 (0.09)	0.01 (0.02)	1.40 (1.56) (1.89, 1.17)	0.06 (0.12) (0.16, 0.05)	0.00 (0.01)	0.00 (0.00)
$6\sigma$	1.14 (1.21) (1.02, 1.29)	-0.01 (-0.00) (0.02, -0.06)	-0.01 (-0.02)	-0.00 (-0.01)	0.28 (0.31) (0.27, 0.32)	0.61 (0.48) (0.68, 0.49)	0.00 (0.01)	0.00 (0.00)
$7\sigma$	0.52 (0.58) (1.01, 0.29)	0.63 (0.53) (0.36, 0.73)	0.02 (0.02)	0.00 (-0.00)	0.13 (0.07) (-0.16, 0.28)	0.70 (0.82) (0.82, 0.68)	0.00 (-0.03)	0.00 (0.00)
$2\pi$		0.72 (0.91) (0.62, 0.90)	0.13 (0.25)	0.02 (0.08)		3.07 (3.09) (3.28, 2.76)	0.04 (0.10)	0.00 (0.01)
$3\pi$		0.77 (0.80) (0.91, 0.78)	0.09 (0.08)	0.01 (0.01)		0.13 (0.20) (0.15, 0.13)	0.01 (-0.05)	0.00 (-0.00)
Total $\sigma$			0.07 (0.09)	0.01 (0.01)			0.01 (-0.01)	0.00 (0.00)
Total			0.29 (0.42)	0.04 (0.10)			0.05 (0.04)	0.00 (0.01)

<sup>a</sup> The figures in parentheses correspond to three cases of deletion: (a) on the first line, all d and f AO's deleted, e.g., 0.21 for  $s_P$  under  $5\sigma$ ; (b) on the second line (left)  $d_P$  and  $f_P$  only deleted, (right)  $d_O$  and  $f_O$  only deleted. <sup>b</sup> The populations of the inner-shell MO's  $1\sigma$  and  $3\sigma$  are 2.00 for  $s_P$ , that of  $2\sigma$  is 2.00 for  $s_O$ , that of  $4\sigma$  is 2.00 for  $s_P$ .

**Table VIII.** Total Energy  $E$  (au) with Full Basis Set<sup>a</sup> and with Various Deletions,<sup>b</sup> for  $N_2$  at 2.0132 au, for  $P_2$  at 3.4974 au, for  $Cl_2$  at 3.8000 au,<sup>c</sup> and for  $F_2$  at 2.68 au

	$-E(N_2)$	$\Delta E(N_2)$	$\Delta E(P_2)$	$-E(P_2)$	$-E(Cl_2)$	$\Delta E(Cl_2)$	$-E(F_2)$	$\Delta E(F_2)$
Full basis set	108.99447			681.50039	919.00610		198.7683	
Delete p from $\sigma_u$	108.87174	0.12273	0.02103	681.47936				
Delete all d, f	108.89955	0.09491	0.09296	681.40743	918.94691	0.05919	198.7418	0.0265
		0.12813	0.02254					
Delete p from $\sigma_u$ and delete all d, f	108.77142	0.22304	0.11550	681.38489				
Delete p, d, f from $\sigma_u$ only	108.84695	0.14751						

<sup>a</sup> Full basis set for  $N_2$ :  $1s$  ( $\zeta = 10.586$  and  $6.037$ ),  $3s$  (7.334),  $2s$  (2.539 and 1.588),  $2p\sigma$  (7.677, 3.270, 1.890, and 1.222),  $3d\sigma$  (2.7878),  $4d\sigma$  (1.5657),  $4f\sigma$  (2.2682),  $2p\pi$  (7.677, 3.270, 1.890, and 1.222),  $3d\pi$  (2.7935),  $4d\pi$  (2.740),  $4f\pi$  (3.3235). <sup>b</sup> For  $N_2$ , "delete p from  $\sigma_u$ " means delete all  $2p\sigma$  STF's from the LCAO expressions for the  $n\sigma_u$  MO's. For  $P_2$ , it means delete the essentially valence-shell STF's  $3p\sigma$  (2.0351, 1.1978, and 0.72) but leave the essentially inner-shell STF's  $2p\sigma$  (6.5053 and 12.50) and  $3p\sigma$  (4.8605); this deletion affects mainly the valence-shell MO  $4\sigma_u$  and affects the inner-shell MO's  $1\sigma_u$ ,  $2\sigma_u$ , and  $3\sigma_u$  only a little.<sup>c</sup> See ref 27a.

Discussion). Table VIII also shows the effect of d and f deletion in  $Cl_2$  and  $F_2$ .<sup>27a</sup> Table IX shows the populations of the s, p, d, and f STF's in the valence-shell MO's of  $N_2$ , both when the full basis set (footnote a of Table VIII) is used and when either the d and f STF's or the  $2p\sigma$  STF's in the  $4\sigma_u$  MO, are deleted.

## Discussion

### (1) The Role of d Functions in Chemical Bonding.

For  $P_2$  and PO, the extents of  $d\sigma$  and  $d\pi$  participation are similar to those found by Boyd and Lipscomb<sup>7a</sup> (see also Boyd<sup>7c</sup> for interesting density contour maps), but the present calculations include additional details. In agreement with Boyd and Lipscomb, the  $d\pi$  is

(27a) NOTE ADDED IN PROOF. See A. C. Wahl, *J. Chem. Phys.*, **41**, 2610 (1964). Note that Wahl's full basis set ( $9 \times 9 \times 5 \times 5$  in his Table IV) is somewhat more restricted than that for  $N_2$  in Table VIII. However, although it contains only one d and one f function, their orbital exponents were optimized. Their coefficients in  $2\sigma_g$  and  $3\sigma_g$  are respectively 0.02 and 0.05 for  $d\sigma$  0.01 and 0.01 for  $f\sigma$ ; in  $1\pi_u$  they are 0.02 for  $d\pi$  and 0.01 for  $f\pi$ .

**Table IX.** Atomic Orbital Populations of Valence-Shell MO's in  $N_2$ <sup>a</sup>

MO	s	p	d	f
$2\sigma_g$	1.419 (1.493)	0.536 (0.507)	0.041	0.004
$3\sigma_g$	0.713 (0.672)	1.352 (1.328)	-0.058	-0.007
Sums	2.132 (2.165)	1.888 (1.835)		
$2\sigma_u$	1.347 (1.492)	0.646 (0.058)	0.008	-0.001
	[2.152] <sup>b</sup>	[0.000] <sup>b</sup>	[-0.123] <sup>b</sup>	[-0.029] <sup>b</sup>
$1\pi_u$		3.864 (4.000)	0.125	0.011
Total $\sigma$	3.479 (3.657)	2.534 (2.343)	-0.009	-0.004
Total		6.398 (6.343)	0.116	0.007

<sup>a</sup> The figures in parentheses refer to calculations in which the d and f functions were deleted. <sup>b</sup> The figures in brackets refer to calculations in which the p functions were deleted from  $1\sigma_u$  (where this contribution is negligible anyway) and  $2\sigma_u$ . Note that the LCAO coefficients of the d and f STF's are greatly increased in magnitude when the p functions are deleted; for the respective STF's  $3d\sigma$  (2.7858),  $4d\sigma$  (1.5657), and  $4f\sigma$  (2.2682), the  $2\sigma_u$  coefficients before deletion are -0.005, -0.004, 0.001, after deletion 0.032, 0.070, and 0.046.

Table X. d and f Populations in Several Molecules<sup>a</sup>

	Cl <sub>2</sub>	P <sub>2</sub>	P in PO	O in PO	N <sub>2</sub>	
4σ <sub>g</sub>	0.030, 0.009	0.046, 0.005	5σ	0.052, 0.008	2σ <sub>g</sub>	0.041, 0.004
5σ <sub>g</sub>	0.049, 0.005	0.033, 0.000	6σ	-0.007, -0.002	3σ <sub>g</sub>	-0.058, -0.007
4σ <sub>u</sub>	0.010, 0.001	0.019, 0.001	7σ	0.023, 0.001	2σ <sub>u</sub>	0.008, 0.000
Total σ	0.089, 0.015	0.098, 0.006	Total σ	0.068, 0.007	Total σ	-0.009, -0.003
2π <sub>u</sub>	0.045, 0.021	0.240, 0.032	2π	0.134, 0.021	1π <sub>u</sub>	0.125, 0.011
2π <sub>g</sub>	0.026, -0.004		3π	0.085, 0.007	Total	0.116, 0.008
Total π	0.071, 0.017		Total π	0.219, 0.028		
Total	0.160, 0.032	0.338, 0.038	Total	0.287, 0.035		

<sup>a</sup> The first entry is for dσ or dπ, the second for fσ or fπ.

size) associated with weaker bonding. The relatively weak dπ participation in Cl<sub>2</sub> tends to disprove the writer's attribution<sup>6</sup> of the greater bond strength of Cl<sub>2</sub> than of F<sub>2</sub> to dπ hybridization. However, d participation in Cl<sub>2</sub> is important energetically (Table VIII), but the difference between Cl<sub>2</sub> and F<sub>2</sub> is not striking.

The relatively strong dπ participation in N<sub>2</sub> (especially energy-wise; cf. Tables III and VIII) may be attributed to strong π overlap due to the small R<sub>e</sub> (relative to atomic size) associated with very strong bonding. The larger d population in P<sub>2</sub> than in N<sub>2</sub> may be attributed to the greater accessibility (lower excitation energy) of the 3d MO in the P than in the N atom. The still greater phosphorus d population (*per P atom*) in PO than in P<sub>2</sub> is as expected in view of the considerable positive charge on the P atom in PO (cf. Table VI).

Coulson<sup>3</sup> has suggested that when the amount of d participation is small one should think of it only as polarization,<sup>21</sup> but that only when it is massive, as especially in compounds of transition elements where the atoms contain d electrons, "is there any really significant chemical meaning in talking about the role of d electrons in bonding." Thus in N<sub>2</sub> and Cl<sub>2</sub> and perhaps also in P<sub>2</sub> one can speak of d participation as polarization. However, in PO, with a d population of 0.29 electron on phosphorus; in SO<sub>2</sub>, with a sulfur atom d population<sup>17,18</sup> of 0.55 or 0.43 electron; and in SO<sub>4</sub><sup>2-</sup> and SF<sub>6</sub> with respective d populations<sup>17</sup> of 0.94 and 1.2 electron, it can be argued that the d participation should be called chemical. In this series of examples, it is seen to be scarcely possible to draw a line anywhere between small and large d participation. Basically, the question can be dismissed as trivial semantics; what is really involved is just the mathematical description of the forms of the MO's, which in themselves are merely convenient expressions for use in one way of building up wave functions of molecules. Still, MO's, and AO's for atoms, are convenient concepts. Granting this, and noting that there is no d participation (except through configuration interaction) in AO's in atoms such as N, O, Cl, P, and S, it can reasonably be argued that all d participation of these atoms *when they enter molecules* can properly be thought of as a chemical effect.

That d participation has an important influence on valence angles in molecules AH<sub>3</sub> and AH<sub>2</sub> has been suggested<sup>5</sup> but not documented by calculations. Of interest are some computations<sup>19</sup> on silylamine (experimentally, N(SiH<sub>3</sub>)<sub>3</sub> is planar), which indicate that d participation in the N atom induces pyramidalization, while addition of d functions on the Si does not much affect the valence angles but does strengthen the bonding, through pπ-dπ back-bonding.

A point which has been emphasized by some people<sup>20</sup> is that certain MO's, because of their symmetry characteristics, can become bonding *only* through d participation in some of their atoms because s and p functions cannot contribute with the right symmetry. For example, in SO<sub>2</sub> the 1a<sub>2</sub> MO becomes bonding by the LCAO combination of a d function of a<sub>2</sub> symmetry with two O atom p AO's. Similarly, in CO<sub>2</sub> the 1π<sub>g</sub> MO has some bonding character through use of a 3dπ STF on the carbon atom in the LCAO form 2pπ<sub>O1</sub> + 3dπ<sub>C</sub> - 2pπ<sub>O2</sub>. In such cases, it is hardly possible to deny that d participation is a chemical effect. But even when symmetry does not require d functions, their participation, small or large, in molecules when absent in the free atoms<sup>23</sup> may reasonably be called a chemical effect.

(2) **The Role of s-p Hybridization in N<sub>2</sub> and P<sub>2</sub>.** The electron configuration of N<sub>2</sub> is 1σ<sub>g</sub><sup>2</sup>1σ<sub>u</sub><sup>2</sup>2σ<sub>g</sub><sup>2</sup>2σ<sub>u</sub><sup>2</sup>-1π<sub>u</sub><sup>4</sup>3σ<sub>g</sub><sup>2</sup>. In simplest LCAO approximation, 1σ<sub>g</sub> is σ<sub>g</sub>1s, 1σ<sub>u</sub> is σ<sub>u</sub>1s, 2σ<sub>g</sub> is σ<sub>g</sub>2s, 2σ<sub>u</sub> is σ<sub>u</sub>2s, 3σ<sub>g</sub> is σ<sub>g</sub>2p, 1π<sub>u</sub> is π<sub>u</sub>2p, where σ<sub>g</sub>1s means σ<sub>g</sub> derived from 1s by the additive linear combination (1s<sub>a</sub> + 1s<sub>b</sub>) of 1s on the two atoms, σ<sub>u</sub>1s is the corresponding subtractive linear combination, and so on. For a minimal basis set, ordinarily a single STF is used for each AO (followed by orthogonalization of the 1s and 2s STF's to make the 1s and 2s AO's). Much better, a minimal set consisting of atomic SCF-AO's can be used. Incidentally, each SCF-AO can be constructed as a linear combination of suitable STF's but let us think in terms of LC-SCFAO-MO's built from best SCF-AO's however arrived at. In the molecule in this approximation, the LCSCFAO forms σ<sub>g</sub>1s, σ<sub>g</sub>2s, and σ<sub>g</sub>2p interact to give the final SCF-MO's.

In the *accurate* MO's, the SCF-MO's are modified by internal changes in their STF coefficients, also by s-p hybridization and by polarization with d and f STF's. The accurate MO is thus expressible in LCMAO form (MAO means modified SCF-AO). However, let us ignore these modifications for the moment.

In terms of LC-SCFAO-MO's using unmodified SCF-AO's there is *forced s-p hybridization* among LCAO forms of like symmetry.<sup>29</sup> This forced hybridization does not affect the AO electron populations, but does introduce negative *overlap* populations of considerable size. As a result, if we may use overlap populations as an index of bonding, the net total bonding effect in N<sub>2</sub> of the pairs of electrons in the σ<sub>g</sub>2s and σ<sub>g</sub>2p.MO's is actually less than if either MO alone

(28) Or their bonding effect in a molecule even if they are present in the free atoms from which it is formed.

(29) R. S. Mulliken, *J. Chem. Phys.*, **23**, 2338 (1955).

were occupied (also, the interaction with  $1\sigma_g$  contributes a further negative effect).<sup>29</sup>

On the other hand, *free s-p hybridization* for the electrons in the  $\sigma_u2s$  MO, resulting from interaction with the unoccupied MO  $\sigma_u2p(3\sigma_u)$ , is available to reduce very greatly the otherwise very strong antibonding effect of the electrons in this MO. (There is, however, a small negative overlap effect due to the forced hybridization between  $\sigma_u2s$  and  $\sigma_u1s$ .) This free hybridization has been termed *isovalent hybridization*,<sup>22</sup> since it occurs without change in the trivalent character of the nitrogen atom (one  $\sigma$  bond, formally from  $\sigma_g2p$  if one assumes the effects of  $\sigma_g2s$  and  $\sigma_u2s$  to cancel each other, and two  $\pi$  bonds).

In an earlier paper,<sup>21</sup> it was suggested that essentially the entire bond energy in  $N_2$  could be attributed to free hybridization in the  $2\sigma_u$  MO, since without it the net effect of  $2\sigma_g2\sigma_u^2$ , which in the approximation  $(\sigma_g2s)^2(\sigma_u2s)^2$  is equivalent to the interaction of two closed shells  $2s^2$  forced closely together, would be an extremely strong repulsion. The results of the calculations reported in Table VIII for  $N_2$  show that this suggestion was to a considerable extent correct: when free hybridization is inhibited and  $2\sigma_u$  is forced to be essentially pure  $\sigma_u2s$  by the omission of all p STF's from the basis set for the  $\sigma_u$  MO's the energy is increased by 0.123 au or 3.35 eV. The effect is larger than that of the omission of d and f STF's from the basis set.

Table VIII shows that an analogous but much smaller effect of free s-p hybridization (0.021 au) exists in  $P_2$ . Here there is a difficulty in that one cannot fully disentangle s-p hybridization in the valence-shell MO  $4\sigma_u$  (which is analogous to  $2\sigma_u$  of  $N_2$ ) from the LCAO structure of the inner-shell  $\sigma_u$  MO's. To provide needed  $\sigma_u2p$  character for the inner-shell function  $3\sigma_u$ , the  $2p\sigma$  basis functions, also  $3p\sigma$  (4.86), were retained and the smaller- $\zeta$   $3p\sigma$  basis functions were omitted in the calculation whose results are reported on  $P_2$  in Table VIII. While this procedure is not quite as clean-cut as one would wish, it is felt to be fairly satisfactory. (In  $N_2$ , the same problem exists, but only to a

very minor extent, in the fact that the omission of  $2p\sigma$  functions from all  $\sigma_u$  deprives  $1\sigma_u$  of its small interest in these functions.)

For an understanding of why  $P_2$  ( $D_0 = 5.03$  eV) is not as stable as  $N_2$  ( $D_0 = 9.76$  eV), and does not form a gas like  $N_2$ , the much smaller effect of free s-p hybridization may be significant. It is also notable that, while d participation is much greater in  $P_2$  than in  $N_2$  if we look at LCAO d coefficients and d populations, the *energetic* effect of d participation is no greater in  $P_2$  than in  $N_2$ . This fact is perhaps a result of the much tighter binding in  $N_2$  due to greater free s-p hybridization.

In the LC-SCFAO-MO approximation discussed above, the sum total AO population in  $N_2$  in the AO's which correspond to the three  $\sigma_g$  MO's  $\sigma_g1s$ ,  $\sigma_g2s$ , and  $\sigma_g2p$  should be exactly 2.00 in each of the AO's  $1s$ ,  $2s$ , and  $2p\sigma$ .<sup>29</sup> Forced hybridization should not change these numbers. But, referring to the computed numbers *in parentheses* in Table IX (using these since we wish here to exclude d polarization), the sum of the s populations in the  $2\sigma_g$  and  $3\sigma_g$  MO's is 2.17 and the sum of the p populations 1.83. (The  $1\sigma_g$  s population, which is 2.00, can safely be taken as essentially  $1s$ .) The discrepancy, if real,<sup>30</sup> as compared with the expectation just stated, can be attributed to a kind of *free hybridization* which may become possible because Table IX is *not* based on LCSCFAO-MO's but on LCMAO-MO's in which the pure  $2s$  and/or  $2p\sigma$  SCF AO's have been modified by some mixing with excited s AO's (doubtless mainly  $3s$ ).<sup>31</sup> Table IX shows that the same kind of free hybridization<sup>30</sup> occurs in  $P_2$ .

(30) Or *possibly* it may be an artifact of the population analysis method, which sometimes gives unacceptable results (e.g., small negative AO populations).

(31) Note that the s population given by the population analysis cannot be attributed unequivocally to  $1s$  and  $2s$ , except that it is safe to attribute very nearly 2.00 to  $1s$ . The remainder should be 2.00  $2s$  SCF-AO's if we were dealing with a pure LCSCFAO approximation, but because it is *modified*, part of this modification is equivalent to the substitution of  $ns$  with  $n > 2$ . (Here compare R. S. Mulliken, *J. Chem. Phys.*, **36**, 3443 (1962), section II.3, where it is pointed out that, in a given central field, an AO with an altered  $\zeta$  is equivalent to an expansion in terms of AO's of that field with varying principal quantum numbers.)