Electron Correlation and the Reality of Xenon Difluoride

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Abstract: The electronic structure of xenon difluoride has been studied using ab initio theoretical methods. The primary goal was to determine whether current theoretical methods are capable of yielding a reasonable value of the dissociation energy of XeF_2. A Slater function basis set of slightly better than "double ζ plus polarization" quality was employed. Four different types of wave functions were investigated: two-configuration SCF, full valence configuration interaction (CI), the first-order wave function, and a larger 1234 configuration wave function including all double excitation from the $10\sigma_g$ orbital. Although the TCSCF symmetric stretching potential curve has both a minimum and maximum, the minimum lies above the comparable energy of separated Xe + 2F. However, the two most complete wave functions predict dissociation energies of 1.97 and 2.14 eV, in qualitative agreement with experiment, 2.78 eV. All four wave functions provide good predictions of the Xe-F equilibrium bond distance. As was the case for KrF_2, the bonding in XeF_2 is found to conform quite closely to Coulson's model $F\ Xe^+\ F^- \leftrightarrow F^-\ Xe^+\ F$ near the equilibrium geometry. The role of the "outer orbitals" 5d and 4f appears to be a quantitative rather than qualitative one.

Xenon difluoride appears to be the simplest known Xe-containing molecule, although there is still some controversy[2] concerning the existence of the XeF radical. As such, XeF_2 plays a special role in the chemistry of the noble gases.[3] XeF_2 was first prepared[4] in 1962, shortly after Bartlett's discovery[5] of $XePtF_6$, and several relatively simple methods of preparation are now available.[3] The dissociation energy for the process

$$XeF_2 \rightarrow Xe + 2F \qquad (1)$$

is ~64 kcal/mol[6] = 2.78 eV. Assuming the value[7] 38.8 ± 2.3 kcal/mol for the dissociation energy D_e of F_2, the molecular dissociation energy for the process

$$XeF_2 \rightarrow Xe + F_2 \qquad (2)$$

is found to be ~25 kcal/mol. For comparison, the smaller KrF_2 molecule is known to lie energetically *above* (by ~15 kcal/mol) the analogous dissociation limit Kr + F_2. This difference between KrF_2 and XeF_2 explains the transient nature of the former as compared to the relative stability of the latter. The geometrical structure of XeF_2 is known from infrared and Raman studies to be linear and symmetric,[3] corresponding to point group $D_{\infty h}$. Reichman and Schreiner[8] have determined the gas-phase Xe-F bond distance to be 1.977 ± 0.002 Å. In the crystalline phase, a neutron diffraction study has yielded 2.00 ± 0.01 for the Xe-F equilibrium separation. Since XeF_2 is a well-characterized species, many other properties[3] have been experimentally determined. However, the dissociation energy and structure are particularly important and of direct relevance to the present theoretical discussion.

The discovery of the existence of noble gas compounds in the early 1960's was viewed in some quarters as an "embarrassment" to theoretical chemistry. However, this would seem an unfair generalization, since only the crudest empirical and semi-empirical theoretical methods could be applied to molecules containing xenon. More recently, Rosen and Ellis[10] have carried out relativistic Dirac-Slater computations on XeF_2 using the $\rho^{1/3}$ local exchange approximation. However, to date the only study of polyatomic xenon compounds which includes exchange exactly appears to be that of Basch, Moskowitz, Hollister, and Hankins[11] on XeF_2, XeF_4, and XeF_6. Their work, although well ahead of its time, use only a small basis set and intentionally concentrated on qualitative features of the electronic structure, wisely making no attempt to predict binding energies relative to the separated atoms and molecules. It now seems well-established[12] that reliable a priori predictions of dissociation energies require (a) basis sets of at least "double ζ plus polarization" quality and (b) explicit treatment of electron correlation, usually by configuration interaction. The development of ab initio theoretical methods has now proceeded to the point where a reasonable theoretical description is quite feasible. Hence the aim of the present study was to determine whether the theoretical methods used successfully in recent years to study "conventional" molecules are capable of providing accurate predictions of the properties of xenon difluoride.

Theoretical Approach

We should state at the outset that the present treatment of XeF_2 is of a nonrelativistic nature. The age-honored justification for the neglect of relativistic corrections is that they affect only the inner shells and hence presumably do not affect the chemistry, which is dictated by the valence electrons. This hypothesis has recently been given some factual support by the work of Schwenzer et al.[13] on the PbO molecule. Nevertheless, the assumption of a nonrelativistic model is without satisfactory theoretical justification and at present must be considered a necessary evil.

The basis set of Slater-type functions is shown in Table I. In the accepted parlance, this basis is of slightly better than "double ζ plus polarization" calibre.[12] The sp basis for fluorine is the "nominal" (4s 3p) basis of Bagus and Gilbert[14] and yields a self-consistent field (SCF) total energy of −99.4081 hartrees, as opposed to the true Hartree-Fock energy, −99.410 hartrees.[14] As seen in Table I, this basis set has been augmented by two 3d and one 4f polarization functions.

For Xe, our basis was modeled after that of Synek and Timmons[15] for Pr^{3+}. The original set (10s 8p 5d) is of double ζ quality except for the 4d functions, of which there are three. Exponent optimization was carried out for the ^1S atomic ground of xenon using the program of Roos et al.[16] The final atomic SCF energy obtained was −7232.1204 hartrees, which may be compared to the numerical Hartree-Fock results of Mann,[17] −7232.14 hartrees, and Fischer,[18] −7232.153 hartrees. Recently Roetti and Clementi[18] have reported a double ζ basis yielding energy −7232.1189 hartrees[19] and a more extended basis yielding −7232.1302

Table I. Basis Set of Slater Functions, $r^{n-1}e^{-\zeta r}$, for Calculations of Xenon Fluorides

Atom	Type	Orbital ζ	Type	Orbital ζ
Xe	1s	55.110	4p	7.422
	1s	36.545	4p	5.036
	2s	26.283	5p	3.516
	2s	22.451	5p	2.016
	3s	14.881	3d	20.469
	3s	12.067	3d	11.964
	4s	7.620	4d	7.727
	4s	5.566	4d	5.233
	5s	3.518	4d	3.379
	5s	2.173	5d	2.0
	2p	30.678	5d	1.2
	2p	21.424	4f	3.5
	3p	13.721	4f	2.5
	3p	10.709		
F	1s	11.011	2p	3.176
	1s	7.917	2p	1.612
	2s	3.096	3d	4.0
	2s	1.946	3d	2.0
	2p	6.165	4f	3.0

Table II. Total Energies (in hartrees) of the XeF_2 Molecule for $D_{\infty h}$ Geometries[a]

R-(Xe–F), bohrs	I TCSCF	II Valence CI	III First order	IV First order + σ doubles
3.4	−7430.9065	−7430.9094	−7430.9843	−7430.9907
3.6	−7430.9293	−7430.9329	−7431.0133	−7431.0197
3.8	−7430.9300	−7430.9342	−7431.0187	−7431.0249
4.0	−7430.9201	−7430.9244	−7431.0108	−7431.0167
4.5	−7430.9053	−7430.9059	−7430.9735	−7430.9764
5.0	−7430.9215	−7430.9216	−7430.9498	−7430.9504
6.0	−7430.9378	−7430.9378	−7430.9458	−7430.9458
8.0	−7430.9405	−7430.9405	−7430.9464	−7430.9464
10.0	−7430.9404	−7430.9404	−7430.9462	−7430.9462

[a] The types of wave functions used are described in the text.

hartrees.[20] Thus it appears that our basis is nearly optimum considering its size and yields an SCF energy within a few hundredths of a hartree of the Hartree–Fock limit. The final xenon basis evolved through the addition of two 5d and two 4f functions, which serve as polarization functions. The polarization functions, with $\langle r \rangle$ values of 2.8, 4.6, 1.3, and 1.8 bohrs, lie in roughly the same region as the xenon Hartree–Fock 4d ($\langle r \rangle = 0.9$), 5s ($\langle r \rangle = 2.0$), and 5p ($\langle r \rangle = 2.3$ bohrs) orbitals.[17] Thus the final basis set includes 95 Slater-type orbitals (STO's), counting $\pi_\pm$, $\delta_\pm$, and $\phi_\pm$ only once.

Four different kinds of wave functions were used in the present work.

I. The two-configuration SCF, TCSCF, wave function required to dissociate to the three SCF atomic wave functions F + Xe + F. Excluding the inner 56 electrons, the two configurations are

$$\ldots 6\sigma_u^2\, 4\pi_u^4\, 3\pi_g^4 10\sigma_g^2\, 5\pi_u^4 \tag{3}$$

$$\ldots 6\sigma_u^2\, 4\pi_u^4\, 3\pi_g^4\, 7\sigma_u^2\, 5\pi_u^4 \tag{4}$$

II. The eight-configuration full-valence configuration interaction (CI), which in addition to (3) and (4) includes

$$4\pi_u^4\, 3\pi_g^4 10\sigma_g^2\, 5\pi_u^4\, 7\sigma_u^2 \tag{5}$$

$$6\sigma_u\, 4\pi_u^4\, 3\pi_g^4\, 10\sigma_g^2\, 5\pi_u^4\, 7\sigma_u \tag{6}$$

$$6\sigma_u^2\, 4\pi_u^4\, 3\pi_g^4\, 10\sigma_g^2\, 5\pi_u^2\, 7\sigma_u^2 \tag{7}$$

$$6\sigma_u^2\, 4\pi_u^4\, 3\pi_g^2\, 10\sigma_g^2\, 5\pi_u^4\, 7\sigma_u^2 \tag{8}$$

$$6\sigma_u^2\, 4\pi_u^2\, 3\pi_g^4\, 10\sigma_g^2\, 5\pi_u^4\, 7\sigma_u^2 \tag{9}$$

$$6\sigma_u^2\, 4\pi_u^3\, 3\pi_g^4\, 10\sigma_g^2\, 5\pi_u^3\, 7\sigma_u^2 \tag{10}$$

III. The first-order wave function,[12,21] including only those configurations in which no more than a single electron occupies an orbital beyond the valence shell, i.e., beyond $7\sigma_u$. Further restrictions invoked here follow. (a) Fifty six electrons are constrained to occupy the innermost two-configuration SCF orbitals in all configurations. (b) The space into which the CI calculations were performed was chosen in a somewhat unusual manner. The occupied TCSCF orbitals ($10\sigma_g$, $7\sigma_u$, $5\pi_u$, and $3\pi_g$) were supplemented by 70 additional MO's. The added MO's were chosen to be single STO basis functions on Xe and symmetric (g or u) combinations of one basis function in each F. This MO set, although it is not orthogonal, spans the full space of the 95 STO basis set. The added MO's which correspond to basis functions describing the atomic ones, Xe 1s to 4s, 2p to 4p, and 3d and F 1s, were deleted (10σ, 4π, and 1δ in all). The remaining MO's were orthogonalized. This process allowed us to reduce the number of configurations in the CI wave function without significant loss of accuracy.

In this way a total of 992 configurations were included in the present first-order wave functions.

IV. In addition to configurations of the type included in the first-order wave function, a further class of configurations has been studied. These configurations are double excitations of the type $10\sigma_g^2 \rightarrow n\sigma\, m\sigma$, or

$$\ldots 6\sigma_u^2\, 4\pi_u^2\, 3\pi_g^4\, 5\pi_u^4\, n\sigma\, m\sigma$$

As discussed by Wahl and Das,[22,23] these configurations have no contribution to the wave function as the molecule dissociates to the three atoms. However, a substantial contribution is possible near the equilibrium internuclear separation, and hence these configurations tend to increase the predicted dissociation energy. Our fourth wave function, which is labeled "first order + σ doubles" here, includes configurations of this type in addition to those present in the conventional first-order wave function, III. A total of 1234 configurations are included in this final wave function.

Wave functions I–III were studied in our earlier study[21] of KrF_2. In addition, it was found that the single-configuration SCF wave function yields a potential curve with its minimum 2.98 eV above the SCF energy of the three atoms F + Kr + F. For this reason, conventional SCF calculations are not reported here for XeF_2. For KrF_2 two-configuration SCF and full-valence CI treatments give essentially indistinguishable results. These wave functions dissociate properly to three SCF atom wave functions, but predict no minimum, only an interesting inflection point, in the symmetric stretching potential curve. Finally, the first-order CI did yield a potential minimum of depth 0.39 eV, as compared with experiment, 1.01 eV. Perhaps even more interesting, a potential maximum of 0.22 eV was found at a larger internuclear separation, 2.42 Å. From a theoretical viewpoint, then, it is of interest to see whether the error in the predicted dissociation energy of KrF_2 is of an absolute (~0.6 eV) or relative nature. Should the latter be the case we would obtain only 40% of the dissociation energy of XeF_2 as well.

Potential Energy Curves

Total energy results are summarized in Table II and Figure 1, which illustrates the potential curves for the symmetric stretching of XeF_2. Predicted bond distances and dissociation energies are given in Table III. Figure 1 does not include wave function II, the eight-configuration valence CI, since as for KrF_2 it is essentially indistinguishable from the TCSCF curve. Note that although there is a potential maximum in the TCSCF potential curve, its minimum lies 0.15

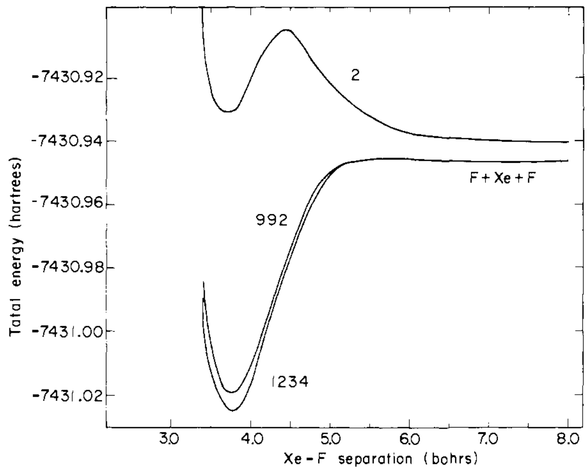

Figure 1. Potential energy curves for the symmetric dissociation of XeF_2 to Xe + 2F. The labels 2, 992, and 1234 refer to the number of configurations included in the different wave functions under study. These wave functions are described in the text.

eV above the dissociation limit F + Xe + F. Thus the TCSCF wave function does not predict XeF_2 to be a thermodynamically stable molecule. However, if one went to the Hartree-Fock limit of a complete basis set, it is probable that XeF_2 would be bound (by perhaps 0.2 to 0.4 eV) in the TCSCF limit. It is also noteworthy that the TCSCF and valence CI wave functions yield predicted Xe-F bond distances within a few thousandths of an ångström of experiment.[7]

The first-order wave function appears to describe XeF_2 in a qualitatively acceptable manner. That is, a substantial dissociation energy is predicted, 71% of the experimental value. This D_e value of 1.97 eV is large enough to guarantee the exothermicity of the process $Xe + F_2 \rightarrow XeF_2$. The absolute error of this D_e, 0.81 eV, is quite comparable to the 0.62 eV error found for KrF_2. The predicted value of r_e(Xe–F) is 0.02 Å longer than the experimental gas-phase result,[7] but curiously in perfect agreement with the crystalline result from neutron diffraction.[9] Of particular interest is the fact that the potential maximum predicted by the comparable calculation on KrF_2 has disappeared in XeF_2. This maximum was due to the ionic nature of the molecule to the left of the maximum and the covalent F Kr F nature to the right. The avoided crossing of these two descriptions results in the potential maximum. It is clear of course that the absence of a potential maximum for XeF_2 does not mean that a shift from covalent to ionic character does not occur. Among other possibilities, the F Xe F covalent curve might just be significantly flatter (less repulsive) than that for F Kr F.

$$F\,Kr^+\ F^- \leftrightarrow F^-\ Kr^+\ F \qquad (11)$$

In our most extensive CI wave function (IV), the first-order wave function is augmented by all double excitations of the type $10\sigma_g^2 \rightarrow m\sigma\, n\sigma$. Both Figure 1 and Tables II and III show that this "first order + σ doubles" wave functions yields a potential curve qualitatively similar to the first-order curve. However, the well is noticeably deeper near the equilibrium geometry and the dissociation energy is 2.14 eV, or 77% of the experiment. Like the first-order prediction, the equilibrium internuclear separation is ~0.02 Å longer than experiment. Thus we conclude that the same methods (including electron correlation)[12] which reliably predict the dissociation energies of conventional molecules are applicable to noble gas compounds. The only real difficulty lies in the fact that the bond energies of noble gas compounds are small and hence are usually exceeded in magnitude by the extramolecular correlation energy. Thus the role of electron correlation is much larger than is usually seen in conventional molecules. Of course in other molecules (e.g., F_2) with small dissociation energies, the same situation will arise.

Table IV. Mulliken Populations for Two-Configuration SCF Wave Functions for Xenon Difluoride

R, bohrs	Xe	F
3.4	52.77	9.62
3.6	52.86	9.57
3.8	52.98	9.51
4.0	53.13	9.44
4.5	53.71	9.15
5.0	53.93	9.04
6.0	53.99	9.01
8.0	54.00	9.00

Electronic Structure Considerations

Of course one of the most fascinating aspects of noble gas compounds is the search for a simple yet correct model of the chemical bonding. In this sense the principal achievement of the earlier work[21] on KrF_2 was to unequivocally establish the validity of Coulson's model[24] of KrF_2, depicted by (11). In addition to the maximum in the symmetric stretching potential curve, it was found[21] that the electric field gradient changes very rapidly as a function of internuclear separation near the position of the KrF_2 potential maximum. The field gradient shifts from a value at larger r(Kr–F) separation appropriate to the Kr atom to one at smaller separations (including r_e) appropriate to the Kr^+ ion.

In the present work on XeF_2 a much simpler route has been followed. Mulliken populations have been obtained from the TCSCF wave functions and are summarized in Table IV. These show that between r(Xe–F) values of 4.0 and 5.0 bohrs, a switch from the covalent

$$F\ Xe\ F \qquad (12)$$

description to the ionic picture of (11) occurs. The changeover does not occur as rapidly as in KrF_2, but is nevertheless a very real change. This change in electronic structure is also seen of course in the TCSCF potential curve in Figure

Table III. Summary of Structural and Energetic Predictions for XeF_2[a]

Property	I TCSCF	II Valence CI	III First order	IV First order + σ doubles	Expt
r_e(Xe–F), bohrs	3.713	3.724	3.781	3.777	
Å	1.965	1.971	2.001	1.999	1.977 ± 0.002[b]
Energy, hartrees	−7430.93100	−7430.93504	−7431.01875	−7431.02502	
Dissociation energy, eV	−0.26	−0.15	1.97	2.14	2.78[c]
kcal/mol	−5.9	−3.4	45.5	49.4	64[c]

[a] The different types of wave functions are described in the text. [b] Reference 7. [c] Reference 6.

Table V. Orbital Energies (in hartrees) and Mulliken Populations for XeF_2 at an Xe–F Separation of 3.8 bohrs[a]

		Xe				2F		
Orbital	Energy	s	p	d	f	s	p	d
$1\sigma_g$	−1224.5139	2.00						
$2\sigma_g$	−189.4574	2.00						
$1\sigma_u$	−177.8993		2.00					
$1\pi_u$	−177.8972		4.00					
$3\sigma_g$	−40.2907	2.00						
$2\sigma_u$	−35.3412		2.00					
$2\pi_u$	−35.3333		4.00					
$4\sigma_g$	−26.2759					2.00		
$3\sigma_u$	−26.2759					2.00		
$5\sigma_g$	−26.2402			2.00				
$1\pi_g$	−26.2370			4.00				
$1\delta_g$	−26.2292			4.00				
$6\sigma_g$	−7.9698	2.00						
$4\sigma_u$	−6.1302		2.00					
$3\pi_u$	−6.1155		4.00					
$7\sigma_g$	−2.9050			2.00				
$2\pi_g$	−2.8969			4.00				
$2\delta_g$	−2.8785			4.00				
$5\sigma_u$	−1.5444		0.07		0.01	1.92	0.01	
$8\sigma_g$	−1.5270	0.13				1.86		
$6\sigma_u$	−1.0277		0.04				0.03	
$9\sigma_g$	−1.0197	1.69		0.01		0.08	0.20	0.01
$7\sigma_u$	−0.7081		0.62		0.01	0.05	1.30	0.02
$4\pi_u$	−0.6629		0.79		0.02		3.18	0.01
$3\pi_g$	−0.6395			0.09			3.90	
$10\sigma_g$	−0.5762	0.14		0.16		0.02	1.62	
$5\pi_u$	−0.4988		3.22		0.01		0.79	−0.01

[a] These results were obtained from a two-configuration SCF wave function.

1. Thus the present ab initio calculations give strong support to Coulson's model of the bonding in XeF_2. It is also interesting to note that the difference between the dissociation energies of XeF_2 and KrF_2, $2.78 - 1.01 = 1.77$ eV, is very close to the difference between the ionization potentials[26] of Xe and Kr (IP(Kr) = 14.00 eV, IP(Xe) = 12.13 eV, and $\Delta IP = 1.87$ eV). In other words the increase in D_e for XeF_2 correlates very closely with the decrease in IP for Xe.

Orbital energies and a detailed Mulliken population analysis[25] are given for r(Xe–F) = 3.8 bohrs in Table V. There we see that most of the molecular orbitals are primarily distorted linear combinations of atomic orbitals. The small populations indicated for the $6\sigma_u$ orbital are due to the fact that this orbital is occupied only in configuration 4. In the TCSCF model neither the $10\sigma_g$ nor the $6\sigma_u$ orbital energies should be interpreted as ionization potentials in the sense of Koopmans' theorem. Note that the $7\sigma_u$ orbital is doubly occupied in both configurations 3 and 4. Incidentally, the coefficients at this geometry of the two configurations in the TCSCF wave function are 0.9835 and −0.1811. At larger separations of course, both coefficients approach $2^{-1/2}$.

A topic of considerable debate in the literature[27-30] is the importance or unimportance of "higher" or "outer" orbitals in the bonding of XeF_2. Specifically, the unconventional nature of noble gas compounds has led some researchers[29,30] to suggest that 5d and 4f orbitals might in some sense be responsible for the existence of molecules such as XeF_2. Note that our basis set (Table I) does include two functions of each of these types. The present Mulliken populations suggest that 20.262 "electrons" reside in d functions, while 0.037 electron may be assigned to f functions. Since 20.00 electrons are assigned to d functions in the $5\sigma_g$, $1\pi_g$, $1\sigma_g$, $7\sigma_g$, $2\pi_g$, and $2\delta_g$ orbitals, only 0.262 can be identified with 5d orbitals. Thus it appears that the importance of 5d and 4f functions is of a quantitative nature as polarization functions.[12] We find little evidence of a qualitative role for these outer orbitals in the bonding.

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References and Notes

(1) (a) IBM Research Laboratory; (b) University of California.
(2) (a) J. R. Morton and W. E. Falconer, *J. Chem. Phys.*, **39**, 427 (1963); (b) D. H. Liskow, H. F. Schaefer, P. S. Bagus, and B. Liu, *J. Am. Chem. Soc.*, **95**, 4056 (1973).
(3) N. Bartlett and F. O. Sladky, "Comprehensive Inorganic Chemistry", Pergamon Press, Oxford, 1973, pp 213–330.
(4) R. Hoppe, W. Dähne, H. Mattauch, and K. M. Rödder, *Angew. Chem.*, **74**, 903 (1972); C. L. Chernick, H. H. Claasen, et al., *Science*, **138**, 3537 (1962).
(5) N. Bartlett, *Proc. Chem. Soc., London*, 218 (1962).
(6) V. I. Pepkin, Y. A. Lebedev, and A. Y. Apin, *Zh. Fiz. Khim.*, **43**, 1564 (1963).
(7) J. J. De Corpo, R. P. Steiger, J. L. Franklin, and J. L. Margrave, *J. Chem. Phys.*, **53**, 936 (1970).
(8) S. Reichman and F. Schreiner, *J. Chem. Phys.*, **51**, 2355 (1969).
(9) H. A. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963).
(10) A. Rosen and D. E. Ellis, *Chem. Phys. Lett.*, **27**, 595 (1974).
(11) H. Basch, J. W. Moskowitz, C. Hollister, and D. Hankins, *J. Chem. Phys.*, **55**, 1922 (1971).
(12) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.
(13) G. M. Schwenzer, D. H. Liskow, H. F. Schaefer, P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, *J. Chem. Phys.*, **58**, 3181 (1973).
(14) P. S. Bagus, T. L. Gilbert, and C. C. J. Roothaan, *J. Chem. Phys.*, **56**, 5195 (1972).
(15) M. Synek and W. Timmons, *Phys. Rev.*, **185**, 38 (1969).
(16) B. Roos, C. Salez, A. Veillard, and E. Clementi, IBM Technical Report RJ 518, August 12, 1968.
(17) J. B. Mann, Los Alamos Scientic Laboratory Report LA-3690, July 1967.
(18) C. F. Fischer, "Some Hartree-Fock Results for the Atoms Helium to Radon", Department of Mathematics, University of British Columbia, January 1968.
(19) C. Roetti and E. Clementi, *J. Chem. Phys.*, **60**, 4725 (1974).
(20) C. Roetti and E. Clementi, *J. Chem. Phys.*, **60**, 3342 (1974).
(21) P. S. Bagus, B. Liu, and H. F. Schaefer, *J. Am. Chem. Soc.*, **94**, 6635 (1972).
(22) G. Das and A. C. Wahl, *J. Chem. Phys.*, **56**, 3532 (1972).
(23) A. C. Wahl and G. Das, *Adv. Quantum Chem.*, **5**, 261 (1970).
(24) C. A. Coulson, *J. Chem. Phys.*, **44**, 468 (1966); see also R. K. Nesbet, *ibid.*, **38**, 1783 (1963).
(25) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
(26) G. Herzberg, "Atomic Spectra and Atomic Structure", Dover Publications, New York, N.Y., 1944.
(27) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).
(28) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).
(29) K. A. R. Mitchell, *J. Chem. Soc. A*, 1637 (1969).
(30) R. C. Catton and K. A. R. Mitchell, *Chem. Commun.*, 457 (1970).