PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Studies in Configuration Interaction: The First-Row Diatomic Hydrides*

Charles F. Bender† and Ernest R. Davidson‡
Chemistry Department, University of Washington, Seattle, Washington 98105

(Received 3 March, 1969)

Molecular properties of the first-row diatomic hydrides, calculated with accurate configuration-interaction wave functions, are presented. Ground-state functions, constructed from approximate natural orbitals, were determined at the equilibrium internuclear separation for each molecule. The basis sets used, were capable of reproducing recently published self-consistent-field energies to within 0.003 hartrees. A minimum of 70% of the correlation energy and an error in the dipole moment of less than 3% were obtained in a systematic study of each molecule. To attain this accuracy, large numbers of singly and doubly excited configurations were used in the wave functions.

INTRODUCTION

Although an accurate configuration-interaction (CI) study of the first-row diatomic hydrides would have been economically impossible to carry out a few years ago, some notable advances have made this type of calculation possible. Besides the increased speed of computers, probably the most useful contribution was Cade and Huo's[1] presentation of the self-consistent-field (SCF) functions for the first-row hydrides. Without these functions, this study would not have been undertaken. Diagonalization procedures, as presented by Nesbet[2] and later modified by Shavitt,[3] make possible fast computation of eigenvalues and eigenvectors for large matrices. Finally, information from the many previous studies using configuration interaction on atoms and molecules has been very helpful in formulating a workable procedure for calculation of accurate wave functions.

Previous calculations on these molecules range in accuracy from Ransil's[4] single-zeta SCF functions through our CI wave functions for lithium hydride[5] and hydrogen fluoride.[6] Very complete reviews of past hydride calculations are given by Cade and Huo[1] and Krauss.[7]

METHOD

Normalized Slater-type orbitals were used in all calculations. Previous calculations have shown[6] a basis set must be complete enough to yield reasonable SCF results. Since our integration programs were designed to handle large blocks of orbitals with equal orbital exponents, the basis sets of Cade and Huo[1] could not be economically used. Rather than undertake a direct SCF-energy optimization, the basis sets used were chosen to minimize, an error function, $\epsilon(f)$, where[8]

$$\epsilon(f) = N - \mathrm{Tr}(S^{-1}n).$$

N being the number of electrons and

$$(S)_{ij} = \int f_i^* f_j \, d\tau$$

$$(n)_{ij} = \int f_i^*(r)\gamma(r,r')f_j(r')\, d\tau d\tau' \; ;$$

f_i is a member of the set f, and $\gamma(r,r')$ is the SCF spinless first-order reduced density matrix, given by

$$\gamma(r_1,r_1') = N \int \phi(r_1,s_1,x_2,\ldots) \times \phi^*(r_1',s_1,x_2,\ldots)\, ds_1, dx_2 \cdots .$$

If the SCF function, ϕ, is constructed from the set g, then

$$\gamma(r,r') = \sum \rho_{ij} g_i(r) g_j^*(r')$$

and the error function can be shown to be

$$\epsilon(f) = N - \mathrm{Tr}(Q^\dagger S^{-1} Q \rho)$$

$$(Q)_{ij} = \int f_i^* g_j \, d\tau \; .$$

One reason for the choice of the quantity ϵ is now obvious; the above equation involves only overlap integrals which can be trivially calculated. A basis set f was chosen which consisted of many powers of r for each orbital exponent, ζ. The optimum ζ for each set was then determined using an optimization technique similar to that outlined by Ransil.[9] Optimization of the quantity ϵ does, in fact, give reasonable SCF results, for example, an error, ϵ, of 7×10^{-5} gave an SCF energy only 0.0003 hartrees above Cade and Huo's[1] value for lithium hydride. As the number of electrons increased, the energy error was somewhat worse since an error of less than 1×10^{-4} for hydrogen fluoride lead to an SCF energy 0.003 hartree above Cade and Huo's value. Although the true-SCF equations were not solved when open-shell molecules were considered, probably all sets are capable of giving an SCF energy within 0.003 hartrees of the published results. Basis functions which, because of symmetry, did not affect the SCF results but were required for correlation corrections, were included in the sets. These functions were chosen to be localized in the same region of space as the orbitals they were correcting.

Analysis of each molecule followed the same procedure. All calculations were carried out at their respective experimental internuclear separations. After a suitable basis set was chosen, all one- and two-electron integrals were computed. For closed-shell systems, the Roothaan[10] SCF procedure was used to define the beginning orbitals. For open-shell systems the pseudo-SCF equations[11] were solved, then a CI wave function including only selected single excitations was formed and the natural orbitals of this function were constructed. The natural orbitals with large occupation numbers were defined to be the "occupied orbitals" for a single-configuration wave function. Although the SCF step is not necessary since our final expansion functions are approximate natural orbitals, the speed of convergence of this method,[5] is directly related to the initial guess to the expansion function. A reasonable first configuration can be helpful in estimating the importance of other configurations.

In the following discussion, a spin configuration ϕ_i^r, is defined to be the rth orthonormal combination of Slater determinants constructed from ϕ_i, the ith product of space orbitals. All possible combinations of Slater determinants were taken which satisfy the conditions

$$S^2 \phi_i^u = S(S+1)\,\phi_i^u ,$$

$$S_z \phi_i^u = S\phi_i^u ,$$

and $\langle \phi_i^r | \phi_i^u \rangle = \delta_{r,u}$.

Earlier results have shown[11] that only the dominant configuration, ϕ_0, and singly and doubly excited space configurations need be included in a CI wave function in order to calculate reasonable energies and other molecular properties. This, of course, is dependent on the accuracy of the single-configuration wave function, ϕ_0. Although effects on molecular properties of higher-order excitations are not necessarily small, the results presented here seem to indicate that these corrections are small compared to those which were calculated. Except for LiH, it was not even economically feasible to include all doubly excited configurations. Space configurations were selected using an energy contribution criterion. For the ith space configuration, ϕ_i, "the average energy contribution," $\epsilon_i^{(2)}$, was defined as

$$\epsilon_i^{(2)} = \frac{1}{k}\sum_{l=1}^{k} \frac{|\langle \phi_i^l | H | \phi_0 \rangle|^2}{\langle \phi_0 | H | \phi_0 \rangle - \langle \phi_i^l | H | \phi_i^l \rangle} .$$

Space configurations ϕ_i were ordered on this contribution and a reasonable number of space configurations were selected ($\leqslant 1000$). These configurations were used in the CI wave function together with ϕ_0 and all single excitations. The wave function was then analyzed into natural (spinless) orbitals. These orbitals were used as expansion basis functions and the above selection process was repeated. In all calculations "convergence" of the natural orbitals was realized in three or fewer iterations. Tests of "convergence" were stabilization of the total energy and other molecular properties. Table I shows the energy convergence for the BH and HF calculations. Clearly the energy had converged in two iterations for both molecules.

TABLE I. Energy convergence of NO-CI wave functions.

	No. of spin configurations	Total energy (hartrees)	Correlation energy (hartrees)
BH-SCF	1	−25.129 64	0.0000
BH-CI-VIRT	678	−25.248 35	−0.1187
BH-CI-NO-1	1313	−25.261 58	−0.1319
BH-CI-NO-2	1123	−25.262 14	−0.1325
No. of possible configurations	(2580)		
FH-SCF	1	−100.0669	0.0000
FH-CI-VIRT	1185	−100.3034	−0.2364
FH-CI-NO-1	1574	−100.3560	−0.2891
FH-CI-NO-2	1517	−100.3564	−0.2895
No. of possible configurations	(8602)		

TABLE II. LiH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ Li	$(\zeta=3.1926)$;
$(2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma, 4f\sigma)$ Li	$(\zeta=0.8492)$;
$(1s, 2s, 2p\sigma, 3d\sigma)$ H	$(\zeta=1.0813)$;
$(2p\pi, 3d\pi, 4f\pi)$ Li	$(\zeta=4.7889$ and $1.2738)$;
$(2p\pi, 3d\pi, 4f\pi)$ H	$(\zeta=1.6220)$;
$(3d\delta, 4f\delta)$ Li	$(\zeta=6.3852$ and $1.6984)$;
$(3d\delta, 4f\delta)$ H	$(\zeta=2.1626)$;
$(4f\phi)$ Li	$(\zeta=7.9815$ and $2.1220)$;
$(4f\phi)$ H	$(\zeta=2.7033)$.

TABLE III. BeH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ Be	$(\zeta=4.0)$;
$(2s, 2p\sigma, 3d\sigma)$ Be	$(\zeta=1.05)$;
$(2s, 2p\sigma, 3d\sigma, 4f\sigma)$ Be	$(\zeta=0.85)$;
$(1s, 2s, 2p\sigma, 3d\sigma)$ H	$(\zeta=1.2)$;
$(2p\pi, 3d\pi, 4f\pi)$ Be	$(\zeta=6.0$ and $1.5)$;
$(2p\pi, 3d\pi, 4f\pi)$ H	$(\zeta=1.5)$;
$(3d\delta, 4f\delta)$ Be	$(\zeta=10.0$ and $2.5)$;
$(3d\delta, 4f\delta)$ H	$(\zeta=2.5)$;
$(4f\phi)$ Li	$(\zeta=14.0$ and $3.5)$;
$(4f\phi)$ H	$(\zeta=3.5)$.

TABLE IV. BH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ B	$(\zeta=5.9343)$;
$(2s, 2p\sigma, 3d\sigma, 4f\sigma)$ B	$(\zeta=1.4784)$;
$(2p\sigma, 3d\sigma, 4f\sigma)$ B	$(\zeta=0.878)$;
$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma, 4f\sigma)$ H	$(\zeta=1.0179)$;
$(2p\pi, 3d\pi)$ B	$(\zeta=7.05)$;
$(2p\pi, 3d\pi, 3p\pi, 4d\pi, 4f\pi)$ B	$(\zeta=1.3)$;
$(2p\pi, 3d\pi, 4f\pi)$ H	$(\zeta=1.5)$;
$(3d\delta)$ B	$(\zeta=9.4)$;
$(3d\delta, 4d\delta, 4f\delta)$ B	$(\zeta=1.3)$;
$(3d\delta, 4f\delta)$ H	$(\zeta=2.0)$;
$(4f\phi)$ B	$(\zeta=1.3$ and $2.5)$.

TABLE V. CH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma)$ C	$(\zeta=5.9395)$;
$(4s, 2p\sigma, 3p\sigma, 3d\sigma)$ C	$(\zeta=1.9364)$;
$(1s, 4s, 3p\sigma, 3d\sigma)$ C	$(\zeta=1.338)$;
$(2p\sigma, 3p\sigma, 3d\sigma)$ H	$(\zeta=1.338)$;
$(1s, 2s)$ H	$(\zeta=1.9364)$;
$(2p\pi, 3p\pi, 3d\pi)$ C	$(\zeta=7.6)$;
$(2p\pi, 3p\pi, 4p\pi, 3d\pi, 4d\pi, 4f\pi)$ C	$(\zeta=1.7703)$;
$(2p\pi, 3p\pi, 4p\pi, 3d\pi, 4d\pi, 4f\pi)$ H	$(\zeta=0.9053)$;
$(3d\delta, 4d\delta)$ C	$(\zeta=9.5)$;
$(3d\delta, 4f\delta)$ C	$(\zeta=2.1)$;
$(3d\delta, 4d\delta, 4f\delta)$ H	$(\zeta=1.2)$;
$(4f\phi)$ C	$(\zeta=2.5)$.

TABLE VI. NH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ N	$(\zeta=6.8526)$;
$(3s, 3p\sigma, 3d\sigma)$ N	$(\zeta=3.1915)$;
$(2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ N	$(\zeta=1.4479)$;
$(1s, 2s, 2p\sigma)$ H	$(\zeta=1.4479)$;
$(2p\pi, 3p\pi, 3d\pi)$ N	$(\zeta=10.2789)$;
$(2p\pi, 3p\pi, 4p\pi, 3d\pi, 4d\pi, 4f\pi)$ N	$(\zeta=2.7492)$;
$(4p\pi, 3d\pi, 4d\pi, 4f\pi)$ N	$(\zeta=1.6763)$;
$(2p\pi, 3p\pi, 3d\pi)$ H	$(\zeta=2.7492)$;
$(3d\delta, 4d\delta, 4f\delta)$ N	$(\zeta=17.142$ and $2.925)$;
$(3d\delta, 4d\delta, 4f\delta)$ H	$(\zeta=2.925)$;
$(4f\phi)$ N and H	$(\zeta=4.875)$.

TABLE VII. OH basis set.

$(1s, 2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ O	$(\zeta=7.0552)$;
$(3s, 3p\sigma, 3d\sigma)$ O	$(\zeta=3.6695)$;
$(2s, 3s, 2p\sigma, 3p\sigma, 3d\sigma)$ O	$(\zeta=1.4938)$;
$(1s, 2s, 2p\sigma)$ H	$(\zeta=1.4938)$;
$(2p\pi, 3p\pi, 3d\pi)$ O	$(\zeta=10.5828)$;
$(2p\pi, 3p\pi, 4p\pi, 3d\pi, 4d\pi, 4f\pi)$ O	$(\zeta=2.6778)$;
$(3p\pi, 4p\pi, 3d\pi, 4d\pi, 4f\pi)$ O	$(\zeta=1.2282)$;
$(2p\pi, 3p\pi, 3d\pi)$ H	$(\zeta=2.6778)$;
$(3d\delta, 4d\delta, 4f\delta)$ O	$(\zeta=17.6838)$;
$(3d\delta, 4d\delta, 4f\delta)$ O and H	$(\zeta=3.401)$;
$(4f\phi)$ O and H	$(\zeta=5.6883)$.

RESULTS

Tables II–VIII give the basis sets used for each molecule. Table IX gives the molecular data for each calculation as well as the number of configurations used in the final wave functions.

Table X gives a comparison of the total energies calculated in this study with SCF calculations, the best previously published results, and the "experimental" results. In all cases except LiH, the results presented here represent the most accurate variational determination of the total energy. Our previous LiH calculation differed in two respects from the present calculation; (a) the previous calculation included not only double excitations but also quadrupole excitations, and (b) elliptical orbitals were used in the first calculations. Elliptical functions cannot be efficiently used for systems with more than one electronic shell. This feature of ETO's was reflected in our hydrogen fluoride results.[6] Although the second difference might have some effect, most of the difference can be ascribed to the effect of higher excitations. Examination

TABLE VIII. FH basis set.

$(1s,\ 2s,\ 3s,\ 2p\sigma,\ 3p\sigma,\ 3d\sigma)$ F	$(\zeta=9.0423)$;
$(2s,\ 2p\sigma,\ 3p\sigma,\ 3d\sigma,\ 4d\sigma,\ 4f\sigma)$ F	$(\zeta=2.7627)$;
$(2s,\ 2p\sigma)$ F	$(\zeta=1.4514)$;
$(1s,\ 2s,\ 2p\sigma,\ 3d\sigma)$ H	$(\zeta=1.2893)$;
$(2p\pi,\ 3d\pi,\ 4f\pi)$ F	$(\zeta=14.479)$;
$(2p\pi,\ 3p\pi,\ 4p\pi,\ 3d\pi,\ 4d\pi,\ 4f\pi)$F	$(\zeta=4.4507)$;
$(2p\pi,\ 3p\pi,\ 3d\pi)$ F	$(\zeta=1.3749)$;
$(2p\pi,\ 3p\pi,\ 3d\pi,\ 4f\pi)$ H	$(\zeta=1.1176)$;
$(3d\delta,\ 4f\delta)$ F	$(\zeta=20.2708$ and $3.64)$;
$(3d\delta,\ 4f\delta)$ H	$(\zeta=2.3333)$;
$(4f\phi)$ F	$(\zeta=26.063$ and $4.68)$;
$(4f\phi)$ H	$(\zeta=3.0)$.

of the first calculation shows a net energy lowering of ~ 0.001 hartrees due to quadrupole excitations.

TABLE IX. Molecular information.

	LiH	BeH	BH	CH	NH	OH	FH
Ground-state symmetry	$^1\Sigma^+$	$^2\Sigma^+$	$^1\Sigma^+$	$^2\Pi$	$^3\Sigma^-$	$^2\Pi$	$^1\Sigma^+$
R_e(a.u.)	3.015	2.538	2.336	2.124	1.9614	1.8342	1.7328
No. of products of space orbitals	722	468	827	672	989	890	1004
No. of configurations	939	1039	1123	1667	3379	2401	1517

TABLE X. Total energy comparisons for first-row hydrides.

Molecule	SCF (Ref. 1)	Best previous	Reference	CI	Experiment (Ref. 1)
LiH	−7.987 31	−8.060 4	5	−8.060 0	−8.071
BeH	−15.153 12	−15.220 7	12	−15.232 4	−15.265
BH	−25.131 37	−25.145 5	14	−25.262 1	−25.290
CH	−38.279 35	−38.279 35	1	−38.439 9	−39.490
NH	−54.978 06	−54.978 06	1	−55.162 0	−55.252
OH	−75.420 83	−75.420 83	1	−75.642 2	−75.780
FH	−100.070 3	−100.257 7	6	−100.356 4	−100.530

TABLE XI. Comparison of dipole moments.

	SCF[13]	CI	Experiment
LiH	6.002	5.853	5.82[a]
BeH	0.282	0.248	
BH	−1.733	−1.470	
CH	−1.570	−1.427	−1.40[16]
NH	−1.627	−1.587	
OH	−1.780	−1.633	−1.66[17]
FH	−1.942	−1.816	−1.82[b]

[a] Reference 14 extrapolated to $n=-\frac{1}{2}$.

[b] R. Weiss, Phys. Rev. 131, 659 (1963).

The BeH results tend to strengthen Chan and Davidson's[12] conclusion that the experimental energy given by Cade and Huo[1] is somewhat too low. Table XI gives the calculated dipole moments. The Table also gives a comparison of the present results with Cade and Huo's[13] dipole moments and the experimental results, when available. Although the correlation energy was from 10 to 30% too small for each molecule, the dipole moments agree quite well with experiment. Remembering that the basis sets were chosen to duplicate the SCF charge density, the differences between the present results and the SCF results can only be attributed to configuration interaction. Most of the effect is due to inclusion of singly excited configurations.[11] Table XII gives the expectation values of selected one-electron operators.

An interesting tool for analysis of a basis set is "the sum of the pair energies." Many authors have felt this sum can be used as an estimate to the "limit of the basis set." Some limitations on the validity of this has been discussed elsewhere.[18, 19, 20] With the final approximate natural orbitals, the pair energies were calculated for a matter of record. For this purpose "pair energy" was defined as the energy improvement

TABLE XII. Calculated expectation values for first-row hydrides. Here $\langle\langle A\rangle\rangle = N^{-1}\sum_i^N \langle A(i)\rangle$, and the positive Z direction for Z, Z_A, and Z_H is from the heavy atom, A, toward the H atom. Z is measured from the midpoint of the line joining A and H. All quantities are in atomic units.

	LiH	BeH	BH	CH	NH	OH	FH
$\langle\langle r_A\rangle\rangle$	1.9572	1.7391	1.5468	1.3531	1.1878	1.0668	0.9612
$\langle\langle r_H\rangle\rangle$	2.5353	2.6224	2.5412	2.3371	2.1623	2.0261	1.9121
$\langle\langle Z\rangle\rangle$	−0.1780	−0.7419	−0.8751	−0.8388	−0.8136	−0.7847	−0.7646
$\langle\langle r_A r_H\rangle\rangle$	4.5470	4.9749	4.3022	3.4380	2.7739	2.3372	1.9866
$\langle\langle X^2+Y^2\rangle\rangle$	1.9980	1.9349	1.6656	1.4381	1.1799	1.0219	0.8613
$\langle\langle Z^2\rangle\rangle$	2.7486	3.2046	2.7834	2.0620	1.6206	1.3237	1.1292
$\langle\langle r_A^{-1}\rangle\rangle$	1.5205	1.7616	1.9716	2.1680	2.3574	2.5376	2.7164
$\langle\langle r_H^{-1}\rangle\rangle$	0.5594	0.5486	0.5448	0.5567	0.5749	0.5928	0.6111
$\langle\langle P_2(\cos\theta_A)/r_A^3\rangle\rangle$	0.0134	0.0329	0.0653	0.0812	0.0525	0.0003	−0.1130
$\langle\langle P_2(\cos\theta_H)/r_H^3\rangle\rangle$	0.0208	0.0366	0.0512	0.0712	0.0941	0.1337	0.1453
$\langle\langle Z_A/r_A^3\rangle\rangle$	0.0286	0.0309	0.0337	0.0317	0.0320	0.0320	0.0326
$\langle\langle Z_H/r_H^3\rangle\rangle$	−0.0815	−0.1240	−0.1516	−0.1895	−0.2269	−0.2614	−0.2993
$\langle\langle r_A^2\rangle\rangle$	6.4824	4.8670	3.7691	2.8463	2.1666	1.7473	1.4163
$\langle\langle r_H^2\rangle\rangle$	7.5560	8.6327	7.8574	6.4094	5.3581	4.6259	4.0660
Charge density at A	13.8740	34.8083	72.6166	126.6094	203.9327	307.2590	445.0811
Charge density at H	0.3829	0.4324	0.4627	0.4531	0.4665	0.4549	0.4300
Spin density at A	0.0000	0.3223	0.0000	0.0426	0.0546	0.0580	0.0000
Spin density at H	0.0000	0.0367	0.0000	−0.0095	−0.0120	−0.0133	0.0000
Field gradient, q_A	−0.0347	−0.2071	−0.6273	−0.9275	−0.5746	0.3190	2.6444
Field gradient, q_H	0.0525	0.1231	0.1704	0.2550	0.3490	0.1857	0.5540
Force on nucleus A	0.0134	−0.0037	0.0940	0.0012	−0.0287	−0.0750	−0.0600
Force on nucleus H	0.0039	0.0009	0.0066	0.0031	0.0046	0.0251	0.0041

TABLE XIII. Natural orbital pair energies first-row hydrides (hartrees).

	LiH	BeH	BH	CH	NH	OH	FH
Single excitations	−0.0002	−0.0013	−0.0008	−0.0052	−0.0132	−0.0073	−0.0018
1σ–1σ	−0.0376	−0.0374	−0.0374	−0.0377	−0.0378	−0.0369	−0.0364
1σ–2σ	−0.0023	−0.0024	−0.0022	−0.0025	−0.0046	−0.0044	−0.0050
2σ–2σ	−0.0341	−0.0329	−0.0356	−0.0315	−0.0120	−0.0126	−0.0107
1σ–3σ		−0.0017	−0.0041	−0.0050	−0.0032	−0.0035	−0.0045
2σ–3σ		−0.0064	−0.0199	−0.0278	−0.0299	−0.0255	−0.0252
3σ–3σ			−0.0492	−0.0282	−0.0300	−0.0329	−0.0336
1σ–1π				−0.0025	−0.0025	−0.0051	−0.0052
2σ–1π				−0.0177	−0.0195	−0.0345	−0.0258
3σ–1π				−0.0239	−0.0178	−0.0384	−0.0461
1σ–$1\pi^*$					−0.0025	−0.0027	−0.0052
2σ–$1\pi^*$					−0.0195	−0.0131	−0.0258
3σ–$1\pi^*$					−0.0178	−0.0198	−0.0461
1π–$1\pi^*$					−0.0098	−0.0311	−0.0618
1π–1π						−0.0166	−0.0166
$1\pi^*$–$1\pi^*$							−0.0166
$\sum_{ij}\epsilon_{ij}$	−0.0740	−0.0808	−0.1484	−0.1768	−0.2069	−0.2771	−0.3646

TABLE XIV. Comparison of pair energies and variational energies.

	$\sum_{ij}\epsilon_{ij}$	E_0[a]	ϵ[b] Variation	E_{corr}[c]	% error in pair correlation energy[d]	% error in variational correlation energy[e]
LiH	−0.0740	−7.9869	−0.0731	−0.083	11	13
BeH	−0.0808	−15.1523	−0.0801	−0.111	27[f]	28[f]
BH	−0.1484	−25.1290	−0.1332	−0.155	5	15
CH	−0.1768	−38.2770	−0.1629	−0.199	10	19
NH	−0.2069	−54.9749	−0.1871	−0.249	13	26
OH	−0.2771	−75.4165	−0.2258	−0.313	11	30
FH	−0.3646	−100.0652	−0.2913	−0.381	5	26

[a] E_0 is the energy of the first natural configuration.

[b] Including single excitations but relative to E_0.

[c] $E_{\text{corr}} = E_{\text{exp}} - E_{\text{SCF}} - E_{\text{R}}$, where E_{R} is the approximate relativistic corrections for the free atoms[18].

[d] $(E_0 + E_{\text{single}} + \sum \epsilon_{ij} - E_{\text{SCF}} - E_{\text{corr}})/E_{\text{corr}}$.

[e] $(E_0 - E_{\text{SCF}} + \epsilon_{\text{var}} - E_{\text{corr}})/E_{\text{corr}}$.

[f] Experiment probably in error.

obtained in a variational calculation considering all configurations formed by replacing a particular pair of space orbitals by the whole set of natural orbitals. Configurations were chosen in the same manner as in the variational calculations. Table XIII gives "the" pair energies calculated with the approximate natural orbitals. Since the SCF equations are not satisfied by the natural orbitals, the energy contribution from all single excitations is not zero and is included in the Table. The numbers in Table XIII have *not* been divided by the number of electron pairs associated with an orbital pair as was done in our previous work.[6] Hence they tend to vary in proportion to the number of electron pairs contained in a pair of orbitals.

Table XIV gives a comparison of the calculated correlation energy, the sum of the pair energies, and the "experimental" correlation energy. Clearly as the number of electrons increases, the difference between the variational correlation energy and the sum of the pair energies increases. This is probably due to the higher excitations included implicitly as unlinked clusters in summing the pairs. Since the number of important quadruple excitations rises like N^4 while the number of pairs rises only like N^2, the relative effect of neglecting quadruple excitations should increase with N. The fact that the pair energy results improve from NH to HF may be

TABLE XV. Some dominant terms in the wave functions.

$CH(^2\Pi)$	$NH(^3\Sigma^-)$	$OH(^2\Pi)$	$FH(^1\Sigma^+)$
$1\sigma^2 2\sigma^2 3\sigma^2 1\pi$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi 1\tilde{\pi}$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 1\tilde{\pi}$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 1\tilde{\pi}^2$
$3\sigma^2 \rightarrow 1\pi 1\tilde{\pi}$	$3\sigma^2 \rightarrow 4\sigma^2$	$3\sigma^2 \rightarrow 4\sigma^2$	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$
$2\sigma^2 \rightarrow 4\sigma^2$	$1\sigma^2 \rightarrow 9\sigma^2$	$1\pi^2 \rightarrow 2\pi^2$	$3\sigma 1\tilde{\pi} \rightarrow 4\sigma 2\tilde{\pi}$
$1\sigma^2 \rightarrow 9\sigma^2$	$1\sigma^2 \rightarrow 11\sigma^2$	$1\pi 1\tilde{\pi} \rightarrow 2\pi 2\tilde{\pi}$	$1\pi 1\tilde{\pi} \rightarrow 2\pi 2\tilde{\pi}$
$3\sigma 1\pi \rightarrow 1\delta 1\tilde{\pi}$	$2\sigma 1\pi \rightarrow 1\delta 1\tilde{\pi}$	$1\sigma^2 \rightarrow 9\sigma^2$	$3\sigma^2 \rightarrow 4\sigma^2$
$2\sigma^2 \rightarrow 6\sigma^2$	$2\sigma 1\tilde{\pi} \rightarrow 1\pi 1\tilde{\delta}$	$3\sigma 1\tilde{\pi} \rightarrow 4\sigma 2\tilde{\pi}$	$1\pi^2 \rightarrow 2\pi^2$
$3\sigma^2 \rightarrow 5\sigma^2$	$1\pi 1\tilde{\pi} \rightarrow 2\pi 2\tilde{\pi}$	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$	$1\tilde{\pi}^2 \rightarrow 2\tilde{\pi}^2$
$1\sigma^2 \rightarrow 11\sigma^2$	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$	$1\sigma^2 \rightarrow 6\pi 6\tilde{\pi}$	$1\pi 1\tilde{\pi} \rightarrow 1\delta 1\tilde{\delta}$
$1\sigma^2 \rightarrow 5\pi 5\tilde{\pi}$	$3\sigma 1\tilde{\pi} \rightarrow 4\sigma 2\tilde{\pi}$	$2\sigma^2 \rightarrow 5\sigma^2$	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$
$3\sigma 1\pi \rightarrow 5\sigma 3\pi$	$3\sigma^2 \rightarrow 6\sigma^2$	$1\sigma^2 \rightarrow 10\sigma^2$	$2\sigma 1\tilde{\pi} \rightarrow 5\sigma 2\tilde{\pi}$
$2\sigma 1\pi \rightarrow 4\sigma 2\pi$	$2\sigma^2 \rightarrow 5\sigma^2$	$2\sigma 1\tilde{\pi} \rightarrow 5\sigma 2\tilde{\pi}$	$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$
$2\sigma 3\sigma \rightarrow 2\tilde{\pi} 1\pi$	$2\sigma^2 \rightarrow 4\sigma^2$	$2\sigma 1\pi \rightarrow 1\tilde{\pi} 1\delta$	$1\sigma^2 \rightarrow 9\sigma^2$
$2\sigma 1\pi \rightarrow 4\sigma 3\pi$	$1\pi 1\tilde{\pi} \rightarrow 1\delta 1\tilde{\delta}$	$3\sigma^2 \rightarrow 6\sigma^2$	$3\sigma^2 \rightarrow 3\pi 3\tilde{\pi}$
$2\sigma^2 \rightarrow 2\pi 2\tilde{\pi}$	$1\pi 1\tilde{\pi} \rightarrow 3\pi 3\tilde{\pi}$	$3\sigma 2\sigma \rightarrow 3\pi 1\tilde{\pi}$	$3\sigma 1\pi \rightarrow 6\sigma 3\pi$
$2\sigma 1\pi \rightarrow 1\delta 2\tilde{\pi}$	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$	$3\sigma 1\tilde{\pi} \rightarrow 6\sigma 3\tilde{\pi}$
$2\sigma 3\sigma \rightarrow 2\pi 1\tilde{\pi}$	$2\sigma 1\tilde{\pi} \rightarrow 5\sigma 2\tilde{\pi}$	$1\pi 1\tilde{\pi} \rightarrow 1\delta 1\tilde{\delta}$	$3\sigma^2 \rightarrow 6\sigma^2$
$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$	$2\sigma 3\sigma \rightarrow 3\pi 1\tilde{\pi}$	$1\pi^2 \rightarrow 3\pi^2$	$1\sigma^2 \rightarrow 7\pi 7\tilde{\pi}$
$3\sigma^2 \rightarrow 4\sigma^2$	$2\sigma 3\sigma \rightarrow 3\tilde{\pi} 1\pi$	$3\sigma^2 \rightarrow 3\pi 3\tilde{\pi}$	$1\pi 1\tilde{\pi} \rightarrow 3\pi 3\tilde{\pi}$
$2\sigma 1\pi \rightarrow 6\sigma 3\pi$	$2\sigma^2 \rightarrow 6\sigma^2$	$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$	$3\sigma 1\pi \rightarrow 3\tilde{\pi} 1\delta$
$3\sigma^2 \rightarrow 2\pi 2\tilde{\pi}$		$1\pi 1\tilde{\pi} \rightarrow 3\pi 3\tilde{\pi}$	$3\sigma 1\tilde{\pi} \rightarrow 3\pi 1\tilde{\delta}$
$2\sigma^2 \rightarrow 7\sigma^2$		$3\sigma 1\tilde{\pi} \rightarrow 6\sigma 3\tilde{\pi}$	$2\sigma^2 \rightarrow 5\sigma^2$
$2\sigma^2 \rightarrow 1\pi 1\tilde{\pi}$		$2\sigma^2 \rightarrow 4\sigma^2$	$1\sigma^2 \rightarrow 10\sigma^2$
$3\sigma^2 \rightarrow 2\pi 1\tilde{\pi}$		$2\sigma^2 \rightarrow 2\pi 1\tilde{\pi}$	$1\pi^2 \rightarrow 3\pi^2$
$3\sigma^2 \rightarrow 1\pi 2\tilde{\pi}$		$3\sigma 1\pi \rightarrow 6\sigma 3\pi$	$1\tilde{\pi}^2 \rightarrow 3\tilde{\pi}^2$
$3\sigma^2 \rightarrow 1\delta 1\tilde{\delta}$		$2\sigma^2 \rightarrow 6\sigma^2$	$2\sigma^2 \rightarrow 3\pi 3\tilde{\pi}$
		$3\sigma 1\tilde{\pi} \rightarrow 3\pi 1\tilde{\delta}$	$1\pi^2 \rightarrow 6\sigma 1\delta$
		$3\sigma 1\pi \rightarrow 1\delta 3\tilde{\pi}$	$1\tilde{\pi}^2 \rightarrow 6\sigma 1\tilde{\delta}$

optimized configurations.

Constructing the energy from the sum of the pair energies appears easier because fewer configurations are involved and the unlinked cluster problem seems to disappear. Before this method is adopted for routine calculations, certain difficulties must be overcome. First, either a very large CI must be done for each pair or else some optimized-configurations method must be solved for each pair. This is more time consuming than the optimized CI on all pairs simultaneously. In the present work, the optimization on the full wave function reduced the number of configurations for each pair to a reasonable level and no further pairwise optimization was attempted. Secondly, the accuracy with which the sum of the pairs approximates the correlation energy varies with a unitary transformation among the occupied orbitals. This may be a defeating defect since, for BH, the canonical SCF pairs gave only 92% of the correlation energy while a unitary transformation between the 2σ and 3σ orbitals improved the result to 97%.[20] Searching for a minimum sum of pair energies through several unitary transformation at several nuclear positions is out of the question. The canonical SCF pairs for most homonuclear diatomic molecules would give better results at small R than at large R, and hence unreliable energy surfaces. Third, the sum of the pairs looks a little too good for the quality of the basis set. Although this is a subjective judgment, it is quite possible that for polyatomic molecules with a much larger number of valence electrons this method will fail completely.

due to the fact that the natural orbitals do not define the pairs which minimize the error in the sum of the pair energies[19, 20] and hence the error may not be a monotonic function in this sequence of molecules. An alternative explanation is that the error in neglecting three-body effects rises as N increases fast enough to mask the decrease in quality of the basis set.

Table XV shows a few of the dominant configurations in some of the wave functions. This Table emphasizes that (a) every pair in the valence shell is strongly correlated and (b) symmetry and the Pauli exclusion principle greatly affect the results. The physical interpretation of some of these configurations has been discussed elsewhere.[21] Each configuration leads to a correlation in the positions of a pair of electrons without much affecting their individual average distributions.

CONCLUSIONS

The wave functions presented here give properties such as the dipole moment more accurately than did the SCF wave functions. This is a major improvement since previous configuration interaction wave functions were only better than SCF for the energy. The increased accuracy was brought about by including single as well as double excitations even though they contributed very little to the energy.

The present results lead to rather pessimistic conclusions regarding the future of CI calculations for obtaining energy surfaces. First of all, many configurations contribute strongly to the correlation energy. Every pair in the valence shell has a large correlation energy and requires two or three configurations to represent it well. Since the configurations used here are optimized (by use of natural orbitals) this conclusion should apply equally well to other optimization procedures such as multiconfiguration SCF. Secondly, excitations beyond singles and doubles contribute 10% of the correlation energy in the neon-like structures. Most of this error is in the valence shell so it cannot be ignored in calculations of interaction energies of atoms. Also, this error arises mainly because of unlinked cluster effects and is intrinsically spread over many configurations in a way that cannot be improved by use of optimized configurations.

Constructing the energy from the sum of the pair energies appears easier because fewer configurations are involved and the unlinked cluster problem seems to disappear. Before this method is adopted for routine calculations, certain difficulties must be overcome. First, either a very large CI must be done for each pair or else some optimized-configurations method must be solved for each pair. This is more time-consuming than the optimized CI on all pairs simultaneously. In the present work, the optimization on the full wave function reduced the number of configurations for each pair to a reasonable level and no further pairwise-optimization was attempted. Secondly, the accuracy with which the sum of the pairs approximates the correlation energy varies with a unitary transformation among the occupied orbitals. This may be a defeating defect since, for BH, the canonical SCF pairs gave only 92% of the correlation energy while a unitary transformation between the 2σ and 3σ orbitals improved the result to 97%.[19] Searching for a minimum sum of pair energies through several unitary transformation at several nuclear positions is out of the question. The canonical SCF pairs for most homonuclear diatomic molecules would give better results at small R than at large R, and hence unreliable energy surfaces. Third, the sum of the pairs looks a little too good for the quality of the basis set. Although this is a subjective judgment, it is quite possible that for polyatomic molecules with a much larger number of valence electrons this method will fail completely.

---

[*] Supported in part by the National Science Foundation.

[†] Present address: Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201.

[‡] Alfred P. Sloan Foundation Fellow.

[1] P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).

[2] R. K. Nesbet, J. Chem. Phys. 43, 311 (1965).

[3] I. Shavitt, private communication.

[4] B. J. Ransil, Rev. Mod. Phys. 32, 245 (1960).

[5] C. F. Bender and E. R. Davidson, J. Phys. Chem. 70, 2675 (1966).

[6] C. F. Bender and E. R. Davidson, J. Chem. Phys. 47, 360 (1967).

[7] M. Krauss, National Bureau of Standards Technical Note No. 438, 1967 (unpublished).

[8] E. R. Davidson, J. Chem. Phys. 46, 3320 (1967).

[9] B. J. Ransil, Rev. Mod. Phys. 32, 239 (1960).

[10] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[11] C. F. Bender and E. R. Davidson, J. Chem. Phys. 49, 4222 (1968).

[12] A. C. H. Chan and E. R. Davidson, J. Chem. Phys. 49, 727, (1968).

[13] P. E. Cade and W. M. Huo, J. Chem. Phys. 45, 1063 (1966).

[14] J. F. Harrison, Ph.D. thesis, Princeton University, 1966 (unpublished).

[15] L. Wharton, L. Gold, and W. Klemperer, J. Chem. Phys. 37, 2149 (1962).

[16] D. H. Phelps and F. W. Dalby, Phys. Rev. Letters 16, 3 (1966).

[17] F. X. Powell and D. R. Lide, Jr., J. Chem. Phys. 42, 4201 (1965).

[18] E. Clementi, J. Chem. Phys. 38, 2248 (1963).

[19] C. F. Bender and E. R. Davidson, J. Chem. Phys. 49, 465 (1968).

[20] C. F. Bender and E. R. Davidson, Chem. Phys. Letters 3, 33 (1969).

[21] E. R. Davidson, in "Sigma Molecular Orbital Theory," edited by O. Sinanoğlu and K. Wiberg (W. A. Benjamin, Inc., New York, 1969) to be published.