Fig. 1. Momentum distribution of photons from positrons annihilating in metal–ammonia solutions, pure ammonia, and pure cesium. The distributions have been normalized to the same amplitude at 5.5 mrad. MNH_3 is a typical liquid–metal–ammonia solution. All other distributions are for solids and were measured close to liquid–nitrogen temperature. The insert shows the difference between the solution and solid ammonia. In the insert all distributions have been renormalized to the same peak height.

while the $CsNH_3$ solution was frozen close to the eutectic (about 17%).[2] Typical data runs accumulated about 20 000 counts per point in the vicinity of the peak. The drastic change produced by removing the solvated electrons is apparent when one realizes that the distribution for solid $NaNH_3$ (0.7%) was identical with that marked MNH_3 prior to freezing. No such change occurs when $CsNH_3$ is frozen. The angular distribution for pure cesium is included for comparison. The central portion of the cesium distribution is closely parabolic indicative of free electron behavior. At angles greater than 5.5 mrad the metal–ammonia curves are coincident with pure ammonia. The pure cesium distribution never completely matches the other curves. The relative heights of the peaks are not very accurate due to normalization at 5.5 mrad where the amplitude is quite low. For better comparison, the background from positrons annihilating in solid ammonia has been subtracted and the difference curves (narrow component in the customary terminology) renormalized to the same height. Note the very close similarity of solid $CsNH_3$ and solid $LiNH_3$.

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Methane as a Numerical Experiment for Polarization Basis Function Selection

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The selection of basis functions for ab initio molecular calculations still seems to be more of an art than a science. This is due primarily to the fact that very complete work has only been done for diatomic molecules.[1] The significantly higher cost of calculations for polyatomic molecules has meant a relative scarcity of data.[2] Furthermore, the optimization of basis sets for polyatomic molecules in situ is too prohibitive to be done routinely and therefore, rules from a few representative cases appear to be the only realistic alternative.

A study was carried out on methane using the MOLE Quantum Chemistry System[3] in order to examine the effect of basis function choice as a precursor to an SCF study of second-row hydrides.[4] The data is of interest in itself, in particular, since it illustrates the comparative value of the various alternatives for SCF-type calculations and probably is valid for extended treatments as well.

Polarization functions are those functions which are necessary to represent the distortion (polarization) of the atom within the molecular environment; they are equivalent to higher angular momentum orbitals than are nominally occupied in the isolated atomic constituents. In the case of methane, the carbon $1s$, $2s$, and
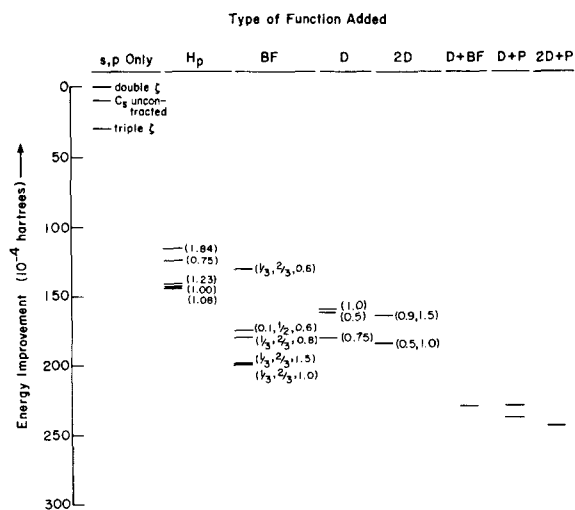

Fig. 1. Effect of polarization function selection for methane

TABLE I. Methane[a] calculations.

	Energy	Improvement ×10⁴	Basis[b]	Comments
Reference calculations				
1.	40.1282		$(2s^21p^1/1s^1)$	Minimal STO optimization
2.	40.1672		$(3s^{10}1p^5/1s^5)$	Whitten[c] double-zeta AO basis
3.	40.1801		$X: (4s^{10}2p^5/2s^5)$	Double-zeta MO basis[c]
4.	40.1833	30	$(5s^{10}3p^5/3s^5)$	Dunning[d] contraction (triple-zeta)
	40.1811	10	$(10s^{10}2p^5/2s^5)$	Carbon s completely free
Carbon d functions				
5.	40.1963	162	$X+d_c(0.5)$	Exponent values for d orbital shown in parentheses;
6.	40.1982	181	(0.75)	Optimum carbon d exponent is 0.74.
7.	40.1961	160	(1.00)	
8.	40.1975	164	$X+d_c(0.9, 1.5)$	
9.	40.1986	185	(0.5, 1.0)	
C–H bond functions				
10.	40.1931	130	$X+BF(1/3, 2/3; 0.6)$	Bond functions placed 1/3 and 2/3 of the distance down the C–H
11.	40.1981	180	0.8	bond from the carbon with identical exponents of 0.6.
12.	40.2000	199	1.0	
13.	40.1999	198	1.5	
14.	40.1976	175	$X+BF(0.1, 1/2; 0.6)$	Bond functions placed 0.1 bohr from carbon and 1/2 the distance down the C–H bond with identical exponents of 0.6, etc.
Hydrogen p functions				
15.	40.1928	127	$x+p_H(0.75)$	Optimum hydrogen p exponent 1.08
16.	40.1943	142	1.00	
17.	40.1944	143	1.08	
18.	40.1942	141	1.23	
19.	40.1916	115	1.84	
20.	40.1983[e]	182	$(5s^{10}5p^5/4s^41p^1)$	
Carbon d functions and C–H bond functions				
21.	40.2031	230	$X+d(1.0)+BF(1/3, 2/3; 1.0)$	
Carbon d functions and hydrogen p functions				
22.	40.2031	230	$X+d_c(1.0)+p_H(1.84)$	
23.	40.2039	238	$X+d_c(0.75)+P_H(1.08)$	
24.	40.2045	244	$X+d_c(0.5, 1.0)+P_H(1.0)$	
Estimated[f] Hartree–Fock limit				
25.	40.225±0.005	400–500		

[a] All methane calculations use a tetrahedral geometry with a C–H distance of 2.0665.
[b] The notation for the basis functions given as $a\ s^b$ means b s-type primitive functions have been grouped to provide a basis orbitals.
[c] Reference 2(b).
[d] Reference 2(l).

[e] Reference 2(c).
[f] Previous estimate of the methane Hartree–Fock limit was given by C. Hollister and O. Sinanoglu [J. Am. Chem. Soc. 88, 13 (1966)] as 40.22. Our analysis agrees with this value. We would estimate the main deficiency in our best calculation (#24) lies in the carbon s, p, and hydrogen s functions.

$2p$ orbitals and the hydrogen $1s$ orbital are nominally the occupied atomic orbitals. Polarization functions available are d, f, g, etc., on carbon and p, d, f, etc., on hydrogen as well as any function located off one of the nuclear centers. This study is restricted to those functions shown most significant[1] in diatomic studies, i.e., (a) $3d$ functions on carbon, (b) $2p$ functions on hydrogen, and finally to (c) bond functions, which in the present work are $1s$-type functions along the C–H bond axis. The reference point for the measurement of

the effectiveness of the various polarization terms was chosen to be a basis set[2(a),2(b),2(d)] that has double-zeta flexibility in the molecule and gave [2(b)] essentially double-zeta results in the carbon atom.

The results are shown in Table I as absolute energies and energies relative to the double-zeta reference calculation. Figure 1 provides a visual illustration of these results. The main conclusions from this data are:

(1) Bond functions provide a reasonable alternative to the more conventional type of polarization functions. In particular, the effect of eight bond functions (calculation No. 12) was not improved on by using fewer than 18 conventional polarization functions (calculation No. 23);

(2) a single d function accomplishes practically all that numerous d functions would;

(3) polarization is added effectively by all three abovementioned techniques [(a), (b), (c)] with hydrogen p's being somewhat less effective (and less economical!);

(4) the use of a second kind of polarization in addition to any one of types [(a), (b), (c)] has about half[5] the energetic contribution it would have had by itself;

(5) the results of various placements of the bond-functions along the bond axis (certainly somewhat arbitrary here) appears to be fairly insensitive to the exact location along the axis;

(6) polarization functions are energetically more important than relaxing the contraction of the s and p functions[6];

We appreciate a number of helpful discussions with Dr. Ralph Young and Dr. Thom Dunning.

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[5] Arrighini et al. (Ref. 2(e)] have carried out an SCF study of methane with $(5s3p1d/2s1p)$ STO basis. Their total energy is almost exactly the same as our $(4s^{10}2p^51d^1/2s^51p^1)$ Gaussian calculation. Their calculation showed an improvement of 167×10^{-4} due to the carbon d functions and 84×10^{-4} due to the hydrogen p functions, and in combination a contribution of 259×10^{-4} (i.e., an almost additive effect). The additive effect is probably due to their orbital exponents being somewhat different from more optimal values (compare with Table I nonoptimal calculations 7, 19, and 22).

[6] Two calculations were done (see Table I) to see if additional flexibility in the s and p basis were of the same order of magnitude as the addition of polarization functions. Dunning's contractions $(5s^{10}3p^5/3s^5)$ [essentially triple-zeta flexibility and an almost saturated carbon s set $(10s^{10}2p^5/2s^5)$] only gave energy improvements an order of magnitude less than use of polarization functions.

Simple Approximate Wavefunctions for Alkali Atoms

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In calculations of cross sections for inelastic collision processes, it is often useful to have simple approximate one-electron wavefunctions for atoms. Slater orbitals,[1] for example, are simple nodeless functions that have been used in a variety of applications.[2] For more accurate work, self-consistent field functions are sometimes applied. However, these have several disadvantages, namely that they are not solutions of simple one-electron Schrödinger equations, and they do not give accurate values for the energy levels of the excited states. In treating the dynamics of charge transfer[3] involving reactions such as

$$Li^+ + Na(3s) \rightarrow Li(n, l) + Na^+ \qquad (1)$$
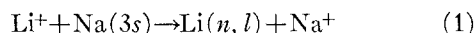
and in excitation by electron impact

$$e^- + Li(2s) \rightarrow e^- + Li(2p), \qquad (2)$$
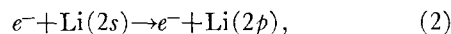
great simplification results from representing Li and Na as $(Li^+ + e^-)$ and $(Na^+ + e^-)$, i.e., as one-electron atoms. The dynamical equations require that the wavefunction for the single electron on the ion satisfy a one-electron Schrödinger equation,

$$H\psi_n = E_n\psi_n, \qquad (3)$$

where

$$H = (-\hbar^2/2m)\nabla^2 + V(r). \qquad (4)$$

Furthermore, it is important[3] that the energy levels of the functions be fairly accurate.

A simple way[4] of doing this is to choose an effective potential for the single electron which depends on the shielding by the inner core electrons as an exponential function of distance:

$$V(r) = -Z_{eff}(\epsilon^2/r)$$
$$= -(\epsilon^2/r)[(Z-1)\exp(-r/\alpha) + 1], \qquad (5)$$

where the effective nuclear charge,

$$Z_{eff}(r) = (Z-1)\exp(-r/\alpha) + 1, \qquad (6)$$

varies from the true nuclear charge Z at $r = 0$, to 1 as