obtained by the dry method may be written $BaPu^{IV}O_3$. The other, obtained by precipitation, could be interpreted as either (i) a PuO_3 compound with barium in a semimetallic bonding state occupying the interstitial position or (ii) a compound of the type Ba_xPuO_3 (with x very small) analogous to sodium and potassium tungstates (Hägg, 1935; Magnéli & Nilson, 1950). Both cubic compounds have space group $Pm3m\,(O_h^1)$ with one molecule per unit cell. In $BaPu^{IV}O_3$ the calculated and observed plutonium oxygen distances were 2·25 Å and 2·18 Å respectively and compared favourably with calculated and observed values of 2·28 Å and 2·20 Å based on the data for $BaU^{IV}O_3$ reported by Russel (oxygen ionic radii taken here as 1·35 Å (Lipson, 1953) and actinide radii taken from Zachariasen, 1954). Similarly in the perovskite of plutonium(VI), the observed distance Pu–O was 2·16 Å, which is identical with the calculated value.

The X-ray data of the orthorhombic phase obtained at 1600 °C are given in Table 1. The phase change from cubic to orthorhombic form could be followed from Roth's diagram showing how the formation of perovskites depends on the ionic radii of A and B elements (Roth, 1957). Considering the ionic radii of barium and plutonium, the point for $BaPu^{IV}O_3$ in the diagram was found to be in the cubic region, but very near the borderline, indicating the possibility of both cubic and pseudocubic systems. The heating of the system probably caused sufficient change to induce a reduction in the coordination number of barium leading to the formation of a pseudo-cubic cell, the true cell being orthorhombic.

Table 1. *X-ray data on* $BaPuO_3$ *(orthorhombic form) obtained at* 1600 °C

The data are indexed with

$a=5·795,\ b=5·861,\ c=5·983$ Å

d (Å)	$q^2{}_o$ (10^{-4})	$q^2{}_c$ (10^{-4})	hkl	I_o
3·392	517	516	111	*vw*
2·991	664	664	002	*s*
2·918	698	698	020	*m*
2·899	707	708	200	*m*
2·423	1012	1014	112	*vw*
2·085	1367	1371	202	*w*
		1359	022	
1·958	1550	1545	212	*w*
1·855	1726	1728	031	*w*
1·751	1938	1932	311	*w*
1·695	2068	2066	222	*w*
1·461	2786	2776	040	*vw*
1·448	2832	2833	104	*vw*
		2832	400	
1·307	3479	3489	240	*w*
1·178	4285	4270	043	*w*

For unreacted BaO and PuO_2 weak lines were also noticed in the pattern, but are not recorded here.

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X-ray scattering factor of a hydrogen atom in a hydrogen molecule.*

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The effective scattering factor f^e of a hydrogen atom in a hydrogen molecule was calculated by McWeeny (1952) with a charge density function based on a Heitler–London wave function

$$\Psi=(1/\sqrt{(2(1+S^2_{AB}))}\{\varphi_A(1)\varphi_B(2)+\varphi_A(2)\varphi_B(1)\}$$

where

$$\varphi_A(1)=\varphi_{1s}(r_{1A})=N_{1s}\exp\,(-\mu r_{1A})\,,$$
$$\varphi_B(2)=\varphi_{1s}(r_{2B})=N_{1s}\exp\,(-\mu r_{2B})$$

and S_{AB} is the overlap integral.

The parameter μ was chosen to be 1 a.u. in McWeeny's calculation, and the magnitude of the effective factor was found to be generally less than that for an isolated hydrogen atom. This fact was interpreted as due to migration of electrons away from the nucleus into the bond.

The authors have evaluated the scattering factor f^e

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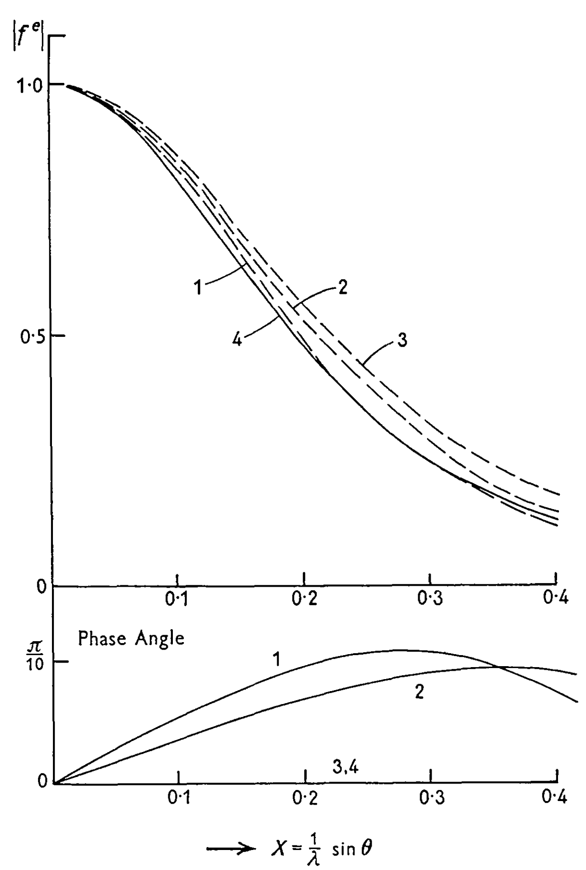

Fig. 1. Magnitude and phase of f^e for H in H_2 by the Weinbaum function. The curves labeled 1, 2, 3 refer to f^e with orientation angles between the bond and the scattering normal, 0, $\pi/4$, $\pi/2$, respectively. Curve 4 refers to f, the scattering factor for the isolated H atom. (The results for the Wang function have been left out because they are very close to the curves for the Weinbaum function presented here.)

using McWeeny's definition with both the Wang (1928) and Weinbaum (1933) wave functions, which are obtained by variation of μ and, in the case of the Weinbaum function, also of a mixing parameter for ionic structures. These functions are regarded as giving fairly good descriptions of the charge distribution in a hydrogen molecule.

Results shown in Fig. 1 reveal that the magnitude of f^e is not necessarily less than that for an isolated atom, and in fact it is more in most cases. This increase of f^e is attributed to the value of μ, which is larger than 1 for both the Wang and Weinbaum functions. Calculations for the case where $\mu = 1$ showed that our work was in agreement with that reported by McWeeny.

Our more exact calculation indicates that the corrections to f^e due to a change in μ are about twice the size of, and in the opposite direction to, those computed by McWeeny. This suggests that in the analysis of X-ray scattering data, in the absence of the molecular wave functions needed to calculate f^e correctly, it would be better to use X-ray scattering factors for spherical atoms rather than X-ray scattering factors calculated according to the method of McWeeny. It should be pointed out that the calculations here are identical with those of McWeeny, except for the use of effective μ values characteristic of the molecule rather than the atom, so that the general utility of McWeeny's approach is affected only by the availability of suitable molecular wave functions.

The fact that the major source of correction to f^e comes from the variation of μ shows the danger in using an atoms-in-molecule approach to the discussion of the effects of electron and X-ray scattering from molecules containing light atoms. It is also clear that the X-rays and electrons in the wave length region usually used in structural analysis work are mainly sensitive to the contraction of the overall size of the electron cloud of the hydrogen atoms in molecular hydrogen as compared with their size in the free state. This can be demonstrated (Bonham & Iijima, 1963) by the fact that the total cross section for the elastic scattering of electrons from a hydrogen molecule is decreased to less than that for two non-interacting hydrogen atoms at the same internuclear separation. This can also be seen by comparing the electron density for two hydrogen atoms separated by a distance of 1·4 a.u. with the electron density given by the first order density matrix for the hydrogen molecule, using either the Wang or the Weinbaum wave function. It is clear from such comparisons that the enhancement of the electron density in the neighborhood of the bond or the nucleus is accomplished by a decrease of density on the side of the nucleus away from the bond, and that the latter effect is the most significant one in the calculation of the corrections to the X-ray scattering factor for atomic hydrogen in molecular hydrogen. Ruedenberg (1962) has also made comments on the importance of size changes accompanying chemical bond formation.

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