The investigation described in this paper was supported by the U.S. Atomic Energy Commission under Contract AT(11-1)-72, Project No. 4.

The authors are indebted to Dr F. H. Spedding, Ames Laboratory of the U.S. Atomic Energy Commission, for the pure rare-earth metals used in this research.

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X-ray Scattering by Aggregates of Bonded Atoms. III. The Bond Scattering Factor: Simple Methods of Approximation in the General Case

By R. McWeeny

Department of Physical Chemistry and Coke Research, University of Durham, King's College, Newcastle-upon-Tyne 1, *England*

(*Received* 5 *September* 1952 *and in revised form* 25 *February* 1953)

General approximate methods of calculating the bond scattering factor (defined in a previous paper) are devised: formulae are given which cover all cases arising from bonds involving (1*s*), (2*s*) and (2*p*) electrons. The approximate method is compared with the earlier rigorous method in a treatment of the hydrogen molecule and is found to be entirely adequate.

The *absolute* accuracy of the resultant effective atomic scattering factor (f^e) is carefully investigated, again in the hydrogen-molecule case, by systematic refinement of the wave function. A change of 'effective nuclear charge' in the atomic orbitals employed is found to have a considerable effect on the calculated f^e, but the introduction of a certain amount of configuration interaction (equivalent to the addition of ionic terms) is found to have a very small effect. It is concluded that the original definition of an effective scattering factor (based upon a one-configuration wave function) is completely satisfactory. More complete knowledge of the parameters in molecular wave functions is perhaps desirable; but calculations based upon quite crude estimates are likely to yield substantially correct scattering factors since the valence-electron contribution is usually relatively small. On the other hand, attempts to allow for the effect of bonding by empirical methods, using point charges in the bonds, are to be discouraged.

1. Introduction

In a preceding paper (McWeeny, 1952, hereafter II) the problem of discussing the scattering of X-rays by a molecule or lattice of *bonded* atoms has been formally solved: the conventional treatment is modified only in so far as the atomic scattering factors are replaced by certain *effective* factors which are obtained from the familiar isolated-atom factors (recently revised by McWeeny, 1951, hereafter I) by addition of appropriate corrections. The corrections incurred involve certain 'bond scattering factors'

$$f(\varrho_{AB}) = \frac{1}{S_{AB}} \int \varphi_A(\mathbf{r_A}) \varphi_B(\mathbf{r_B}) \exp\{i\varkappa \mathbf{S}.\mathbf{r}\} d\mathbf{r} \,, \quad (1)$$

and although an accurate and fairly general method of computing these quantities was developed in II, it is evident that calculations along these lines would become excessively laborious in elaborate applications; indeed, even in the case of the hydrogen molecule (II) the labour involved effectively precluded a full examination of the dependence of the results upon accuracy of the wave function.

In this paper a simple *approximate* method of evaluating the bond scattering factor is developed: the example treated in II is then re-examined for purposes of comparison and the new method is found to be entirely adequate. Briefly the method consists of replacing the hydrogen-like or Slater (1930)* atomic orbitals occurring in (1) by approximate expressions of more suitable analytical form: the integration may then be effected in simple closed form without any of the tedious expansions required by the original, accurate method. Satisfactory approximations to (1*s*), (2*s*) and (2*p*) orbitals follow in § 2 and make possible the treatment of all bonds between atoms from hydrogen to neon; there should be no difficulty in extending the method to heavier atoms but it seems clear that

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* The Slater functions are nodeless, one-term functions with a radial factor $r^n \exp\{-ar\}$.

the effect of bonding will become relatively less important with increasing atomic number and for this reason attention will be confined to the orbitals mentioned above (including, of course, linear combinations or 'hybrids').

2. The Gaussian approximation

The value of Gaussian functions in constructing orbitals which are more accurately based upon hydrogen-like or Slater functions has been recognized elsewhere (McWeeny, 1949, 1950; Boys, 1950); in spite of the somewhat inferior accuracy of simple Gaussian approximations they may often be manipulated much more easily than their more conventional counterparts. In the present application we shall employ such functions simply as a means of approximating Slater orbitals, so that the scattering integrals (1) may be reduced by substituting the Gaussian forms of φ_A, φ_B.

The Slater functions (unnormalized), and typical Gaussian terms from which corresponding approximations may be built, are given in Table 1.

Table 1

	$(1s)$	$(2s)$	$(2p)$
Slater:	$\exp\{-Zr\}$	$r\exp\{-Zr/2\}$	$(\mathbf{r}.\hat{\boldsymbol{\delta}})\exp\{-Zr/2\}$
Gaussian:	$\exp\{-ar^2\}$	$r^2\exp\{-a'r^2\}$	$(\mathbf{r}.\hat{\boldsymbol{\delta}})\exp\{-a''r^2\}$

$\hat{\boldsymbol{\delta}}$ is a unit vector along the $(2p)$ orbital.

The Slater functions, which are invariably made the starting point in molecular calculations and which are certainly accurate enough for our purposes (estimation of a bond *correction*), are themselves *exact* eigenfunctions of a certain central-field problem: for the $(1s)$ and $(2p)$ functions this field is simply that of an 'effective point charge', Z, the electronic potential energy then being $V(r) = -Z/r$, while for the $(2s)$ function it is such that $V(r) = -Z/r+1/r^2$. Our Gaussian functions will be rather less satisfactory than the Slater functions, but we shall ensure that they approach the latter by making them approximate solutions of the *same eigenvalue problem*. More specifically, we shall replace a Slater function (ψ) by a suitable (normalized) combination of Gaussian terms (ψ_v, say) and vary all the parameters until the integral $E_v = \int \psi_v H \psi_v d\mathbf{r}$ reaches its lowest value, H being the Hamiltonian operator, $H = -\frac{1}{2}\nabla^2+V(r)$. By the variation theorem, the resultant ψ_v is the 'best' approximation to ψ, of its kind, in the sense that E_v is then the closest estimate of E in the eigenvalue equation $H\psi = E\psi$. First and second approximations to each Slater function have been constructed in this way by using, respectively, one and two Gaussian terms. The results, for a general effective charge Z (which appears simply as a scale factor), are collected in Table 2.

The accuracy of the functions is reflected in that of the eigenvalues (the errors are 2·8, 7·1 and 1·3% respectively) but more important for our purposes is the *range* over which the Slater functions are closely fitted. It might, in fact, be argued that since the accuracy of E_v is of no direct consequence to us these functions are not necessarily the best for our purposes. But let us compare our approximations with the Slater functions. Fig. 1 shows clearly that, while the one-term approximation is very poor, addition of a second Gaussian term effects an enormous improvement, leaving a substantial failure only in the region fairly near the nucleus: poor estimates of energy are to be associated with this residual failure at small distances. In all cases, however, the (two-term) approximations are satisfactory over the broad 'middle range'; this is to be expected since the greater portion of the integral for E_v arises from this region and consequently variational correction of ψ_v first effects the most significant improvement in this range. Now we are using our functions to approximate a bond density, $\varrho_{AB} = \varphi_A\varphi_B/S_{AB}$, and it is clear that it is precisely the *middle regions* of the functions which are in the main responsible for the accuracy of this approximation. Fig. 1 makes this more obvious, for the vertical lines H and C indicate, on the scale of the figure, the position of the second nucleus in the hydrogen molecule and in diamond respectively. In all cases the two-term approximations should give a ϱ_{AB} which is satisfactory except in the vicinity of the nuclei (where one of its factors fails). Moreover, these regions of failure comprise only a minor part of the bond charge cloud and the density there is in any case very small. It therefore seems likely, at the outset, that our method of approximation should meet with considerable success.

Unlimited accuracy could, of course, be obtained by taking more Gaussian terms but the variational procedure would then become unwieldy as a means of selecting best values of the many parameters and it might be preferable to resort to curve-fitting methods. At the same time, this aspect of the investigation should be kept in true perspective; it would be foolish to strive for wave functions of a precision quite out of keeping with the rather general issues at stake.

In the test case of a later section the integral (1), defining the bond factor, is found to be rather insensitive to the precise form of the orbitals employed

Table 2. *Gaussian approximations to Slater orbitals for effective nuclear charge* Z; $\boldsymbol{\rho} = Z\mathbf{r}$

	1-term	2-term
$(1s)$	$2{\cdot}765\times 10^{-1}.Z^{3/2}\exp\{-0{\cdot}2829\varrho^2\}$	$2.426\times 10^{-1}.Z^{3/2}(\exp\{-1{\cdot}330\varrho^2\}+0{\cdot}725\exp\{-0{\cdot}2014\varrho^2\})$
$(2s)$	$3{\cdot}114\times 10^{-3}.Z^{3/2}\varrho^2\exp\{-0{\cdot}05016\varrho^2\}$	$1{\cdot}493\times 10^{-2}.Z^{3/2}\varrho^2(\exp\{-0{\cdot}2037\varrho^2\}+0{\cdot}190\exp\{-0{\cdot}04685\varrho^2\})$
$(2p)$	$2{\cdot}928\times 10^{-2}.Z^{3/2}\boldsymbol{\rho}.\hat{\boldsymbol{\delta}}\exp\{-0{\cdot}04468\varrho^2\}$	$4{\cdot}109\times 10^{-2}.Z^{3/2}\boldsymbol{\rho}.\hat{\boldsymbol{\delta}}(\exp\{-0{\cdot}1512\varrho^2\}+0{\cdot}392\exp\{-0{\cdot}03287\varrho^2\})$

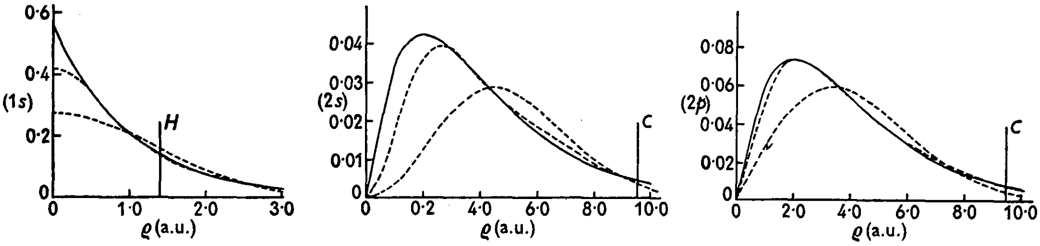

Fig. 1. One- and two-term Gaussian approximations to Slater (1*s*), (2*s*) and (2*p*) functions. The vertical lines at *H* and *C* indicate, on the appropriate scale, the position of a second nucleus in the hydrogen molecule and in diamond respectively.

(φ_A, φ_B). Even the very crude, one-term function is not without value as a means of roughly (but very rapidly) estimating the effect of bonding, while the two-term function gives results almost indistinguishable from those calculated (II) using the true Slater functions. This suggests strongly that there is no need to use more than two Gaussian terms: the functions given in Table 2 should be generally valid and are adapted to any particular problem simply by inserting the appropriate Z value (using Slater's rules); they are reasonably accurate in the range of special interest and undoubtedly represent a satisfactory compromise between high accuracy and general convenience.

3. The general evaluation of bond factors

We shall now show that the bond scattering factor for any type of bond involving the orbitals dealt with in § 2 may be easily evaluated in closed form; the same treatment can be extended to more general cases if necessary.

First consider the integral

$$(a|f|b) = \int \exp\left(-ar_A^2\right) \exp\left(-br_B^2\right) \exp\left(i\varkappa \mathbf{S}.\mathbf{r}\right) d\mathbf{r}\,, \quad (2)$$

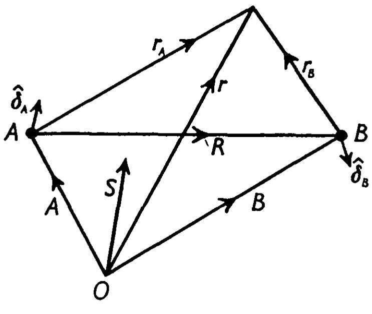

Fig. 2. Notation used in calculating the bond factor for a bond *A–B*, referred to an arbitrary origin *O*.

the notation being as in Fig. 2. The single Gaussian terms from which the approximations to (1*s*), (2*s*) and (2*p*) orbitals are constructed may be denoted by

$$(1s, a) = \exp\left\{-ar_A^2\right\}, \; (2s, a') = r^2 \exp\left\{-a'r_A^2\right\},$$
$$(2p, a'') = \mathbf{r}.\hat{\boldsymbol{\delta}} \exp\left\{-a''r_A^2\right\},$$

so that the approximations become,

$$(1s) = \sum_r A_r(1s, a_r), \; (2s) = \sum_r A_r'(2s, a_r'),$$
$$(2p) = \sum_r A_r''(2p, a_r'')\,.$$

With a similar notation, the integral (2) may be denoted more fully by $(1s, a|f|1s, b)$ where the information in the first and final brackets relates to the orbitals on centres A and B respectively. The corresponding many-term approximation to a bond scattering factor involving (1*s*) orbitals on atoms A and B would be $(1s|f|1s) = \sum_{r,s} A_r B_s (1s, a_r|f|1s, b_s)$.* Similarly $(2s|f|2s) = \sum_{r,s} A_r' B_s' (2s, a_r'|f|2s, b_s')$ etc., and it therefore suffices to evaluate the terms involving single Gaussian orbitals.

Now if we denote the integral (2) by I it follows that $(2s, a|f|1s, b) = -(\partial I/\partial a)$, $(1s, a|f|2s, b) = -(\partial I/\partial b)$, $(2s, a|f|2s, b) = (\partial^2 I/\partial a \partial b)$, so that all scattering integrals involving only (2*s*) orbitals may be derived by differentiating I (which we shall see may be evaluated in closed form) with respect to the parameters a, b.

In order to deal with the (2*p*) orbitals it is convenient to introduce vectors $\mathbf{A}' = \mathbf{A} + \boldsymbol{\delta}_A$, $\mathbf{B}' = \mathbf{B} + \boldsymbol{\delta}_B$, where $\boldsymbol{\delta}_A = \delta_A \hat{\boldsymbol{\delta}}_A$ and $\boldsymbol{\delta}_B = \delta_B \hat{\boldsymbol{\delta}}_B$ ($\hat{\boldsymbol{\delta}}_A$ and $\hat{\boldsymbol{\delta}}_B$ being unit vectors) are vectors pointing along the directed (2*p*) orbitals at A and B, and to denote by I' the integral (2) in which $\mathbf{A}, \mathbf{B}$ are replaced by $\mathbf{A}', \mathbf{B}'$. It then follows easily that

$$(2p, a|f|1s, b) = \frac{1}{2a}\left(\frac{\partial I'}{\partial \delta_A}\right)_{\delta_A, \delta_B \to 0},$$

$$(1s, a|f|2p, b) = \frac{1}{2b}\left(\frac{\partial I'}{\partial \delta_B}\right)_{\delta_A, \delta_B \to 0},$$

$$(2p, a|f|2p, b) = \frac{1}{4ab}\left(\frac{\partial^2 I'}{\partial \delta_A \partial \delta_B}\right)_{\delta_A, \delta_B \to 0},$$

$$(2p, a|f|2s, b) = -\frac{1}{2a}\left(\frac{\partial^2 I'}{\partial \delta_A \partial b}\right)_{\delta_A, \delta_B \to 0},$$

so that all the scattering integrals involving (2*p*) orbitals may also be derived from the single integral (2).

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* If the orbitals on A, B are similar, $A_r = B_r$, $a_r = b_r$. Generally this is not so and in what follows we denote the parameters on the two sides of f simply by a and b.

We shall now evaluate (2) and list for convenience the final expressions for the various integrals. The only necessary result is

$$\int \exp\left(-pr^2+\mathbf{q}.\mathbf{r}\right)d\mathbf{r} = \frac{\pi^{3/2}}{p^{3/2}}\exp\left\{\frac{q^2}{4p}\right\}$$

which may be proved in the general case (in our application the vector q has *complex* components) by separating the integrand into x, y, z factors and evaluating each of these by integration round a suitable contour.

We then obtain

$$I = \frac{\pi^{3/2}}{(a+b)^{3/2}} \times \exp\left\{\frac{-4ab(\mathbf{A}-\mathbf{B})^2+4i\varkappa'(a\mathbf{A}+b\mathbf{B}).\hat{\mathbf{S}}-\varkappa'^2}{4(a+b)}\right\}, \qquad (3)$$

where $\hat{\mathbf{S}}$ is the unit vector along $\mathbf{S}$ and $\varkappa' = \varkappa S$.

Putting $(\mathbf{B}-\mathbf{A}) = \mathbf{R}$, $(\varkappa'/4\pi) = X$, and with ψ as the angle between $\mathbf{S}$ and the bond, we then find, on differentiating and carrying out the limiting processes,

$$\begin{aligned}
(2s, a|f|1s, b) &= -IG_a\,,\\
(1s, a|f|2s, b) &= -IG_b\,,\\
(2s, a|f|2s, b) &= I[G_aG_b+G_{ab}]\,,\\
(2p, a|f|1s, b) &= (1/2a)IG_{\delta_A}\,,\\
(1s, a|f|2p, b) &= (1/2b)IG_{\delta_B}\,,\\
(2p, a|f|2p, b) &= (1/4ab)I[G_{\delta_A}G_{\delta_B}+G_{\delta_A\delta_B}]\,,\\
(2p, a|f|2s, b) &= -(1/2a)I[G_{\delta_A}G_b+G_{\delta_A b}]\,,\\
(2s, a|f|2p, b) &= -(1/2b)I[G_aG_{\delta_B}+G_{a\delta_B}]\,,
\end{aligned}$$

where each G-function is of the form $(K+LX^2)+iMX$ and

$$\begin{array}{lll}
K_a = \dfrac{-(2b^2R^2+3\overline{a+b})}{2(a+b)^2} & L_a = \dfrac{4\pi^2}{(a+b)^2} & M_a = \dfrac{-4\pi bR\cos\psi}{(a+b)^2}\\[2ex]
K_b = \dfrac{-(2a^2R^2+3\overline{a+b})}{2(a+b)^2} & L_b = \dfrac{4\pi^2}{(a+b)^2} & M_b = \dfrac{4\pi aR\cos\psi}{(a+b)^2}\\[2ex]
K_{ab} = \dfrac{3\overline{a+b}-4abR^2}{2(a+b)^3} & L_{ab} = \dfrac{-8\pi^2}{(a+b)^3} & M_{ab} = \dfrac{-4\pi(a-b)R\cos\psi}{(a+b)^3}\\[2ex]
K_{\delta_A} = \dfrac{2ab\mathbf{R}.\hat{\boldsymbol{\delta}}_A}{(a+b)} & L_{\delta_A} = 0 & M_{\delta_A} = \dfrac{4\pi a\hat{\mathbf{S}}.\hat{\boldsymbol{\delta}}_A}{(a+b)}\\[2ex]
K_{\delta_B} = \dfrac{-2ab\mathbf{R}.\hat{\boldsymbol{\delta}}_B}{(a+b)} & L_{\delta_B} = 0 & M_{\delta_B} = \dfrac{4\pi b\hat{\mathbf{S}}.\hat{\boldsymbol{\delta}}_B}{(a+b)}\\[2ex]
K_{\delta_A\delta_B} = \dfrac{2ab\hat{\boldsymbol{\delta}}_A.\hat{\boldsymbol{\delta}}_B}{(a+b)} & L_{\delta_A\delta_B} = 0 & M_{\delta_A\delta_B} = 0\\[2ex]
K_{\delta_A b} = \dfrac{2a^2\mathbf{R}.\hat{\boldsymbol{\delta}}_A}{(a+b)^2} & L_{\delta_A b} = 0 & M_{\delta_A b} = \dfrac{-4\pi a\hat{\mathbf{S}}.\hat{\boldsymbol{\delta}}_A}{(a+b)^2}\\[2ex]
K_{a\delta_B} = \dfrac{-2b^2\mathbf{R}.\hat{\boldsymbol{\delta}}_B}{(a+b)^2} & L_{a\delta_B} = 0 & M_{a\delta_B} = \dfrac{-4\pi b\hat{\mathbf{S}}.\hat{\boldsymbol{\delta}}_B}{(a+b)^2}
\end{array}$$

Important special cases occur when the $(2p)$ orbitals point along or perpendicular to the bond axis: thus for a π-type bond

$$\hat{\boldsymbol{\delta}}_A.\hat{\boldsymbol{\delta}}_B = 1\,, \quad \mathbf{R}.\hat{\boldsymbol{\delta}}_A = \mathbf{R}.\hat{\boldsymbol{\delta}}_B = 0\,.$$

Finally it is worth noting that when $\varphi_A = \varphi_B$ the bond charge density ϱ_{AB} is symmetrical about the mid-point and consequently $f(\varrho_{AB})$, *referred to this point as origin*, is a real quantity. The calculations are slightly simplified by this observation since, with this origin, the terms occur in conjugate pairs. The contribution, $f_A(\varrho_{AB})$, to the atomic factor f_A^e, is then obtained from $f(\varrho_{AB})$ on multiplication by the phase factor $\exp(2\pi iX\mathbf{R}.\hat{\mathbf{S}})$ (cf. II).

4. Accuracy of the Gaussian approximation

An accurate evaluation of the integral (1) has already been made in the case of the hydrogen molecule (II). At this point it is not our intention to discuss the *absolute* accuracy of the bond factor so calculated, since this depends on the choice of wave function. The actual *calculation* cited was, however, carried through quite rigorously and may, therefore, be used as a standard in estimating the accuracy of the approximation techniques developed in the last two sections. A discussion of the *absolute* accuracy of the bond scattering factor and of the effective atomic factor will be given subsequently (§ 5).

The bond factor $f(\varrho_{AB})$ has been calculated using both one- and two-term Gaussian approximations to the hydrogen $(1s)$ functions. From these approximations the effective atomic factor f_A^e is then constructed according to the method of II. The results are summarized in Figs. 3 and 4, where the various estimates of $f(\varrho_{AB})$ and $f^e_{(A)}$ are shown for two orientations of the molecule, $\psi = 0$ and $\psi = \frac{1}{2}\pi$.

Naturally the calculations based on the single-term Gaussian function are quite seriously in error: the main inadequacy of this approximation is probably its failure to recognize the marked asphericity of the bond charge, which in this approximation is effectively replaced by a more diffuse spherical distribution. The poor approximation to $f(\varrho_{AB})$ is reflected in the corresponding f^e curves, but it is worth noting that both the general effect of bonding and the predicted differences between the factors for various orientations are essentially accounted for. Physically this would suggest that the general disposition of electronic charge is more important than the precise *shapes* of the distribution into which it is resolved: this is particularly true when there is strong interference between the different (atom- and bond-) scattered beams (as in the case $\psi = 0$).

The two-term results are much more satisfactory, as would be expected from an inspection of the function itself (Fig. 1). The effect of asphericity of the bond charge is well reproduced and the final correction of the isolated-atom factor leads to an effective factor which, on the scale of Fig. 4, is indistinguishable from that calculated by the rigorous method of II. The phase shift, which is probably more sensitive to inaccuracies*, is also well accounted for. The case $\psi = \frac{1}{4}\pi$ has also been treated, with equal success, but the corresponding curves are omitted in the interests of clarity.

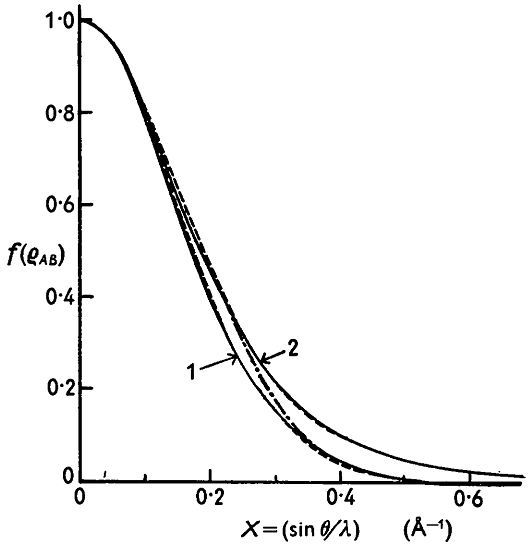

Fig. 3. Approximations to the bond factor. The curves 1 and 2 refer to the cases $\psi = 0$, $\psi = \frac{1}{2}\pi$. The solid curves are accurate while the one- and two-term Gaussian approximations are indicated by ·—·—· and – – – – respectively. The one-term approximation fails to distinguish the two curves 1 and 2.

Now the hydrogen molecule provides the severest possible test of the adequacy of our calculations, for in more complicated molecules, where the atoms possess inner shells, the effect of bonding is relatively less important. It therefore appears that the Gaussian method of evaluating the bond factor will generally be entirely adequate for our purposes. It is perhaps worth remarking that the complete calculation of f^e for hydrogen, using the two-term approximation, can easily be made in a day as compared with several weeks when using the rigorous method of II; moreover, the economy of the Gaussian method increases as the functions become more complex.

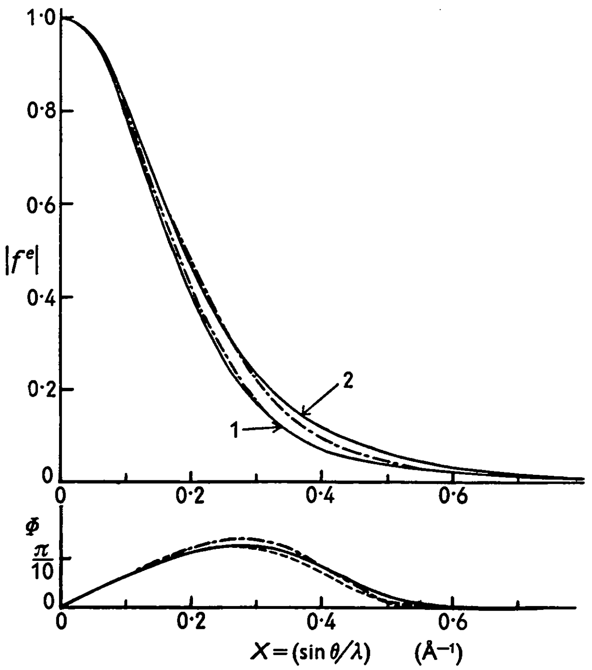

Fig. 4. Magnitude and phase of the atomic factor, f^e. The solid curves are accurate while approximations are indicated as in Fig. 3. Curves 1 and 2 again refer to cases $\psi = 0$, $\psi = \frac{1}{2}\pi$. The two-term approximations to $|f^e|$ are indistinguishable from the accurate curves.

5. Absolute accuracy of $f(\varrho_{AB})$ and f^e

We are now in a position to examine in some detail the approximations upon which our calculations have so far been based. The only fundamental assumption upon which the formal definition of an effective scattering factor (II) is based, is that a one-configuration approximation (i.e. a single determinant formed from a suitable set of atomic and molecular orbitals) adequately represents the true wave function. It is well known that such a function over-emphasizes the probability of finding two electrons simultaneously on a given atom; in the language of valence bond (VB) theory we should say that ionic structures are re-

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* The one-term approximation breaks down completely in the case $\psi = \frac{1}{4}\pi$ but the higher approximation is generally satisfactory.

presented in the wave function with too great a weight. A second assumption, of a more provisional nature, concerned the precise choice of valence orbitals out of which to build the molecular orbital: it was suggested (I) that the parameters (e.g. effective nuclear charge) appropriate to the free atom might be carried over unchanged into the molecular calculations. It is easy to examine the limitation imposed by this second assumption by repeating the calculation for the hydrogen molecule, using modified atomic orbitals (AO's) corresponding to an effective nuclear charge $Z=1{\cdot}193$* instead of the isolated atom AO's ($Z = 1$).

(i) *Effect of change of* AO *parameters*

Reference to Fig. 5, which is best compared with Fig. 3 of II, shows that the refinement of using an effective nuclear charge $Z = 1{\cdot}193$ makes a substantial alteration in the character of the results: for now f^e is nearly always *greater* than f (often by as much as 50%), in complete contrast with our previous predictions. Whilst the qualitative features are preserved, it would appear that the *absolute* value of f^e cannot be given with any confidence unless the AO parameters *appropriate in the molecule* are known with fair accuracy. The reason for the marked change is physically clear: the increased effective charge in the molecule implies a considerable 'shrinkage' in the AO's concerned, and this in turn leads to a greater concentration of charge in the region of the nuclei (and the axis) and a corresponding broadening of the scattering curves. Indeed, to a first approximation the effect results in a change of scale along the X-axis (of the $f^e(X)$ curves) in the ratio of the original and modified effective charges (i.e. in this case almost 20%). Now there is at present very considerable uncertainty about the most suitable values of AO parameters in MO's; the analogy with the case of the hydrogen molecule has lead to the suggestion that exponents should be increased by about 20% when an AO is used in a bonding MO (e.g. Coulson & Duncanson, 1942). There are, however, grounds for believing that in H_2 (the only case of molecular bonding with (1*s*) orbitals) the 20% increase is quite exceptional and that the appropriate changes to be made in cases of (2*s*) and (2*p*) bonding might not exceed 5%.

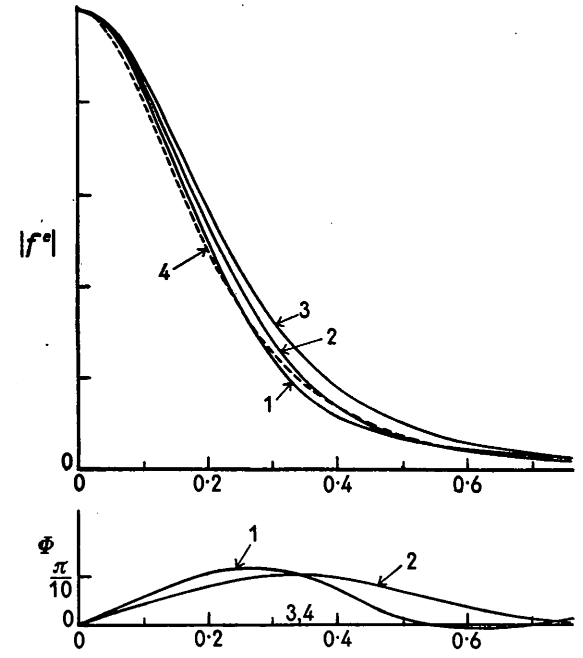

Fig. 5. Magnitude and phase of the atomic factor, f^e, in the higher approximation (§ 5). Curves 1, 2, 3 refer to orientations $\psi = 0$, $\frac{1}{4}\pi$, $\frac{1}{2}\pi$, while 4 is the isolated-atom factor, f.

(ii) *Effect of configuration interaction*

In the present case (the hydrogen molecule) it is not difficult to refine the wave function by adding new configurations (i.e. determinants containing excited-state MO's) and allowing them to mix with the single configuration, used so far, in such proportions as achieve the lowest possible variational energy value. The function so far used as a first approximation to the ground state, namely

$$\Psi = \begin{vmatrix} \psi_g(1)\alpha(1) & \psi_g(1)\beta(1) \\ \psi_g(2)\alpha(2) & \psi_g(2)\beta(2) \end{vmatrix}, \quad \psi_g = \varphi_A+\varphi_B\,,^*$$

might thus be refined by adding a small proportion of

$$\Psi' = \begin{vmatrix} \psi_u(1)\alpha(1) & \psi_u(1)\beta(1) \\ \psi_u(2)\alpha(2) & \psi_u(2)\beta(2) \end{vmatrix}, \quad \psi_u = \varphi_A-\varphi_B\,,^*$$

which would similarly be a first approximation to an excited state with both electrons in the anti-bonding orbital ψ_u. Now if the function $\Psi+\lambda\Psi'$ is expanded it turns out to be simply the variation function chosen by Weinbaum (1933), in which the well known Heitler–London function is supplemented by ionic terms representing both electrons on the same nucleus. This interpretation of the Weinbaum function was pointed out by Coulson & Fischer (1949) and shows that the main failure of the single-configuration MO function (over-emphasis of the ionic terms) may be corrected by admitting higher configurations.

Using the MO method, it would be possible to modify the definition of f^e (II), without introducing prohibitive difficulties, in order to admit interaction with a small number of configurations. This is because the MO's, at least in principle, are solutions of a self-consistent field problem and as such are mutually orthogonal (as assumed throughout these papers). But our knowledge of the extent of such interaction is, as yet, scanty, and if a substantial revision of the (one-

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* This is the most suitable value according to a variational calculation.

* Not normalized.

configuration) charge distribution and corresponding f^e should prove necessary there would be little prospect of making calculations in any but the simplest cases.

The best choice of parameters in the function $\Psi+\lambda\Psi'$ follows from Weinbaum's calculation. Use of this function reduces the absolute error in the variational energy value corresponding to the single determinant (Ψ) by almost a half and it seems safe to conclude that the difference between f^e(MO) and f^e(Weinbaum) is of the same order as the absolute error in f^e.

The results of the final calculation of f^e are extremely gratifying: the curves of Fig. 5 (f^e(MO)) are practically unchanged by configurational interaction, the general effect being to raise the plotted values by, on the average, about 2%. A generous estimate of the average *absolute* error of the f values might be about 5%.

6. Concluding remarks

We may now profitably summarize our finding. The original MO definition of an effective atomic scattering factor f^e is entirely satisfactory; in this approximation the scattering from the valence electrons is resolved into contributions from charges q_A on the atoms (A) and q_{AB} in the bonds (A–B), these atom- and bond-charges being smeared out with (normalized) densities ϱ_A and ϱ_{AB}. Our main concern so far has been with the scattering from the bond density ϱ_{AB}, whose calculation provided the main obstacle to progress; this difficulty has now been resolved by introducing Gaussian approximations to the various wave functions.

The absolute accuracy of the *valence*-electron contribution to f^e appears to be of the order 5% in the case of H_2. In more general applications this figure may be raised somewhat by our ignorance of the most suitable values of AO parameters, but at the same time the valence-electron contribution becomes an increasingly less significant fraction of the whole f^e. The main effects of chemical bonding may, therefore, confidently be predicted by the methods so far developed. For a lattice of atoms *at rest* a complete solution of the scattering problem would appear to be in sight. Unfortunately, in practice, the issue is always complicated by vibrational effects (e.g. vibrational anisotropy) which still cannot be properly estimated. We must, therefore, be prepared to make further changes in f^e (as indeed is the practice with the simpler f's), but these will now be almost* entirely vibrational in origin. In other words, we shall have achieved the primary object of *separating off*, with adequate accuracy, the hitherto obscure effects of interatomic interactions.

The extension of the treatment to more elaborate cases involves no new features beyond the calculation of the atom and bond charges. The definition of these quantities (McWeeny, 1951) is quite general and they may be estimated for polyatomic (including conjugated) molecules and for solids, either by self-consistent MO techniques (at least, in principle) or by the cruder semi-empirical MO method† (i.e., in solids, by the 'tight-binding' approximation). However roughly these estimates may be made it seems likely that in most cases they give a fairly good picture of the general disposition of charge, being, therefore, satisfactory for our purpose. At the same time it seems necessary to remark that this method of dividing up the valence-electron charge distribution provides absolutely no theoretical justification for the practice of 'allowing for' the bonds by placing empirically adjusted *point* charges at the mid-points (e.g. Franklin, 1950; Bacon, 1952). It is essential that the bond charges should be those defined above and that they should be properly *spread out* each according to a density function ϱ_{AB}. Localization of q_{AB} corresponds, in effect, to retention of only the first term in a slowly convergent expansion of the bond factor in powers of X; inclusion, for instance, of a second term leads to quite absurd results, bearing out our contention that the point-charge approximation is quite meaningless. Of course, it is always possible to say that *for a certain reflexion* (i.e. for one particular **S** vector) the scattering from the bond density is equivalent to that from a certain point charge, for any f-curve merely tells us the fraction of a unit point charge e to which the distribution is equivalent, as a function of ($\sin\theta/\lambda$). But this is an obvious evasion of the problem, for widely *different* point charges would be required to account for the different reflexions, corresponding to the fact that the actual bond factor is a complicated function of orientation and scattering angle.

My thanks are due to Prof. G. S. Rushbrooke for kindly reading the manuscript of this paper.

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* The small corrections to f, based on the diffuse valence-electron distribution, are almost certainly relatively insensitive to vibration.

† The overlap integral between adjacent AO's must, of course, be included.