ANGULAR TERMS IN THE ELECTRON DENSITY FOR THE PHOSPHINE MOLECULE

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ABSTRACT. An attempt is made to calculate the first few angular terms in an expansion of the electron density for the phosphine molecule in Legendre polynomials. Such an expansion is appropriate for a model in which the three hydrogen nuclei are smeared to form a circular line charge. The Thomas–Fermi approximation has been used in conjunction with the variational method. The variational density employed includes p and f angular terms. An approximate charge density map is constructed for a plane containing the molecular axis in order to demonstrate the effect of the angular terms.

1. *Introduction.* Quantitative calculations giving electron distributions and potential fields in polyatomic molecules have been carried through in only a very small number of cases. Full wave-mechanical treatments present many mathematical difficulties, and it is therefore of interest to examine any alternative methods of obtaining information of significant accuracy. One such method is that due to Thomas and Fermi, and in recent years a considerable amount of progress has been made in applying this approximation to polyatomic molecules. It is appropriate here to review briefly the work previously carried out in this field. As far as we are aware, the first direct attempt to obtain an approximate solution of the fundamental Thomas–Fermi (T.F.) equation for a polyatomic molecule was concerned with benzene (March (9)). In this work an extension of a method proposed earlier by Hund (8) for dealing with the diatomic molecules N_2 and F_2 was used. Following this a somewhat general method of treating molecules with tetrahedral and octahedral symmetry was developed in the approximation in which the nuclear field is averaged over all orientations about the central nucleus (March (10)). Later a numerical solution of the T.F. equation for methane, in which this averaging is not invoked, was given by Glazer and Reiss (7). Even in this calculation, which was carried out on a high-speed computer, it was necessary to simplify the problem. This was accomplished by first constructing the pyramids formed by the planes bisecting the HCH bond angles. Each pyramid encloses a C—H bond and is replaced by a cone of equal volume. This leads to a problem having axial symmetry, with boundary conditions to be imposed on the surface of the cone. More recently Brinkman and Peperzak (5) (see also Brinkman (4)) have considered approximate analytical solutions of the T.F. equation and have given electron density contours for the water molecule. Examination of the results for atoms indicates that no very high accuracy is achieved in this case and for molecules there appear to be additional uncertainties. We therefore feel that further work is essential before a critical assessment of the reliability of these analytical methods can be made.

In the present paper on the phosphine molecule we shall use an extension of the method developed previously for tetrahedral and octahedral molecules and particularly

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for methane, silane and germane (March (10); Ballinger and March (1)). The basic idea in this work was to treat the electrons as though they moved in a central field, obtained by smearing out the hydrogen nuclei over the surface of a sphere, as Buckingham, Massey and Tibbs (6) had done previously when calculating a Hartree self-consistent field for methane. The natural extension of this method to phosphine is to consider the electrons as moving in the field of the phosphorus nucleus and of a circular line charge, corresponding to the smearing out of the three protons. Using this model we shall attempt to calculate the first few angular terms in the expansion of the electron density in Legendre polynomials. We feel that such a calculation is of considerable interest, since it ought to give some idea of the overall distribution of electrons in the molecule and also the results will be in a particularly suitable form for use in a wave-mechanical calculation. With regard to the latter point it has been shown recently by Banyard and March (3) that the results of experiments on X-ray scattering from a series of ten-electron molecules, including ammonia, can be understood in terms of central field wave functions. This was taken to imply that such wave functions were leading to a density which is a good approximation to the actual density when averaged over angles. The next step in improving the wave functions thus found for ammonia is to remove the central field restriction. In the present paper a more accurate field is obtained for phosphine, and it will not be too difficult to extend the present treatment to ammonia or to any molecule of the type XH_3.

2. *Outline of approach and formulation of basic equations.* The fundamental problem is to solve the T.F. equation

$$\nabla^2 V = \mu V^{\frac{3}{2}}, \quad \mu = \frac{32\pi^2 e}{3h^3}(2me)^{\frac{3}{2}}, \tag{1}$$

for the electrostatic potential V when the nuclear potential V_N is due to a point charge Ze and a circular line charge of total charge Ne (in phosphine $Z = 15$, $N = 3$). This can be written (see, for example, Smythe (12))

$$V_N(\mathbf{r}) = \begin{cases} \dfrac{Ze}{r} + \dfrac{Ne}{R}\sum_{n=0}^{\infty}\left(\dfrac{r}{R}\right)^n P_n(\cos\theta)\,P_n(\cos\alpha) & \text{if} \quad r \leqslant R, \\ \dfrac{Ze}{r} + \dfrac{Ne}{R}\sum_{n=0}^{\infty}\left(\dfrac{R}{r}\right)^{n+1} P_n(\cos\theta)\,P_n(\cos\alpha) & \text{if} \quad r > R, \end{cases} \tag{2}$$

where the notation can be seen by referring to Fig. 1 and the quantities P_n are the Legendre polynomials. The electron density n, having axial symmetry with the model assumed here, can also be expanded in Legendre polynomials, and our task in the present paper is to calculate the first few terms in such an expansion. The problems with which we are confronted are to calculate the radial parts of the separate angular terms and to impose the boundary conditions. Obviously when we limit ourselves to the calculation of a few angular terms the boundary conditions can only be imposed approximately.

It seems to us, therefore, that the most satisfactory method is to base the entire calculation on the variational principle of the T.F. theory, which can be stated in the following way. Let us suppose that we have a density of electrons $n(\mathbf{r})$ which is correctly

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normalized and which satisfies the necessary physical conditions of the problem. From this density we can calculate an electronic potential $V_e(\mathbf{r})$ by solving Poisson's equation. We then form the quantity E defined by

$$\mathrm{E} = c_k \int n^{\frac{5}{3}} d\tau - e \int n V_N d\tau - \tfrac{1}{2} e \int n V_e d\tau + U_N, \tag{3}$$

where $c_k = \dfrac{3h^2}{10m}\left(\dfrac{3}{8\pi}\right)^{\frac{2}{3}}$ and U_N is the nuclear-nuclear interaction energy. If we now require that E shall be stationary with respect to small variations in n, we find that

$$4\pi n e = \mu V^{\frac{3}{2}},$$

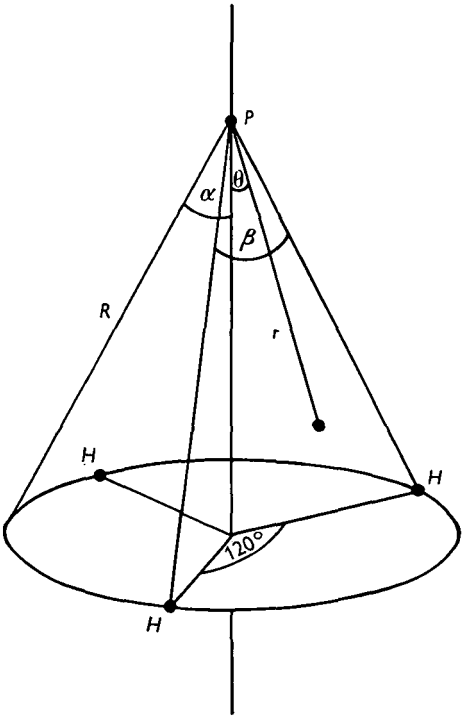


Fig. 1

where $V = V_e + V_N$, the usual T.F. relation between density and potential for neutral systems. Combining this with Poisson's equation leads to the basic equation (1). If this correct T.F. density is inserted into equation (3), the quantity E becomes just the T.F. total energy $E_{\mathrm{T.F.}}$. On the other hand, if we use an approximate density we obtain a value of E which depends on the choice made but which is always higher than $E_{\mathrm{T.F.}}$.

We now base our treatment on this principle and write our approximate variational density in the form

$$n = n_0 + \sum_{l=1,2,3} f_l P_l, \tag{4}$$

where n_0 and f_l are of course simply functions of r. We have retained only three angular terms; it will, however, be clear to the reader that much of the method as developed in this paper is rather general and we describe it in terms of our own particular calculation

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for simplicity. Since over a large part of the molecule the phosphorus nucleus provides a predominant field of force having spherical symmetry, it seems reasonable to assume that the first term, n_0, in this approximate density will, in general, be large compared with the angular terms, although this is obviously not correct in the immediate vicinity of the line charge. It suggests, however, that we set up an explicit variational density of the form (4) by substituting the approximate density in the T.F. equation, written for convenience in terms of the density n rather than the potential V as

$$\nabla^2 n^{\frac{2}{3}} = (4\pi e\mu^2)^{\frac{1}{3}} n.$$

If we treat the angular terms as small and equate coefficients of P_0 (constant), P_1, P_2 and P_3, then it is easy to obtain the following approximate equations, which we shall take as the defining equations for the quantities n_0 and f_l in equation (4):

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{\frac{3}{2}}}{x^{\frac{1}{2}}}, \tag{5}$$

$$\frac{d^2\chi_l}{dx^2} = \chi_l\left[\frac{3}{2}\left(\frac{\phi}{x}\right)^{\frac{1}{2}} + \frac{l(l+1)}{x^2}\right] \quad (l = 1, 2, 3). \tag{6}$$

Here we have introduced the functions ϕ and χ_l defined by

$$n_0 = \frac{\mu}{4\pi e}\left(\frac{Ze}{r}\phi\right)^{\frac{3}{2}}, \tag{7}$$

$$f_l = \frac{3}{2}\frac{\mu}{4\pi e}\left(\frac{Ze}{r}\phi\right)^{\frac{3}{2}}\frac{\chi_l}{\phi}, \tag{8}$$

and x is related to r by

$$r = \left(\frac{3}{32\pi^2}\right)^{\frac{2}{3}}\frac{h^2}{2me^2Z^{\frac{1}{3}}}x = bx.$$

It is easy to see that to this approximation the spherical density n_0 is just that which has already been exhaustively discussed (March (10)) in connexion with tetrahedral molecules. It is of course not surprising that this is so, for in obtaining the approximate equations we have assumed that the angular terms are small, and it can be shown that the density n_0 obtained from equation (5) is the best possible spherical density in the sense of the variational method. In order to see this, reference should be made to the discussion of Ballinger and March (2) for tetrahedral and octahedral molecules; the arguments obviously apply immediately to the present case when we observe that the first term in the expansion of the nuclear potential given in equation (2) is just

$$V_N(r) = \begin{cases} \dfrac{Ze}{r} + \dfrac{Ne}{R} & \text{if} \quad r \leqslant R, \\ \dfrac{Ze}{r} + \dfrac{Ne}{r} & \text{if} \quad r > R. \end{cases} \tag{9}$$

Of course, once n_0 is normalized the approximate density (4) also normalizes because the angular terms contribute nothing to the total charge when they are integrated over the whole of space.

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The procedure is now to obtain approximations to the radial parts governing the angular terms by solving the equations (6). It will be seen that the equations defining f_l are linear and when we require suitable behaviour at the origin and at infinity it turns out that these functions are each determined apart from a simple multiplier. We must then choose these undetermined constants by minimization of the total energy in order to make this density as accurate as possible in the sense of the variation method. Thus the problem is formulated in variational language and we discuss below the results we have obtained.

3. *Detailed results for phosphine.* In the phosphine molecule, according to the data of Nielsen (11), $R = 1{\cdot}424$ Å and $\beta = 93° 50'$ (see Fig. 1). Of the solutions of equation (5) previously tabulated (March (10)) the last solution in Table 1 corresponds to a value of R differing from the experimental value by only 1·4 %. This solution will therefore be used in the calculation of n_0 and χ_l. At the outset of this investigation we decided to adopt a value of 90° for β. This corresponds to a value of α given by $\cos^{-1} 1/\sqrt{3}$, and if we now examine the term in P_2 in the nuclear potential (2) we find that its coefficient is identically zero. This suggests that a term in P_2 in the variational function will be of little importance, and in fact exploratory calculations we have carried out confirm this view completely. We shall therefore drop the P_2 term and simply solve for χ_1 and χ_3. To do this it is necessary to develop a series for χ_l around the origin, in order to calculate starting values for a numerical integration which is extended as far as X (defined by $R = bX$). An asymptotic series for large x was then developed and the solution extended inwards by numerical integration. The continuity of χ_l is then easily imposed since we are dealing with a linear equation.

The variational density is now determined apart from two arbitrary constants entering as simple multipliers in the P_1 and P_3 terms. The next step in applying the variational method is to calculate the electronic potential $V_e(\mathbf{r})$ created by our assumed density. This potential must satisfy the conditions that V_e is finite at the origin, that V_e and grad V_e are everywhere continuous and that V_e tends to zero at infinity as r^{-1}. It is then possible to express the solution as

$$\left.\begin{aligned} V_e &= \frac{Ze}{r}(\phi-1)-\frac{Ne}{R}+\frac{Ze}{r}\sum_{l=1,3}\chi_l P_l-\frac{Ze}{b}\sum_{l=1,3}\frac{1}{(2l+1)}\left(\frac{r}{R}\right)^l[\chi_l'(X)_- - \chi_l'(X)_+]P_l \quad (r\leqslant R),\\ V_e &= \frac{Ze}{r}(\phi-1)-\frac{Ne}{r}+\frac{Ze}{r}\sum_{l=1,3}\chi_l P_l-\frac{Ze}{b}\sum_{l=1,3}\frac{1}{(2l+1)}\left(\frac{R}{r}\right)^{l+1}[\chi_l'(X)_- - \chi_l'(X)_+]P_l \quad (r>R), \end{aligned}\right\} \tag{10}$$

as can be verified after some calculation.*

Here the difference between the slopes at X has to be determined numerically from the solution of equation (6). We must then substitute in the energy integrals to obtain E as a function of the two parameters involved in χ_1 and χ_3. The potential-energy integrals are easily dealt with. We can split the potential energy quite unambiguously into two parts, one arising from the spherical density n_0 and the other due to the angular terms. The first contribution can be obtained immediately from the formulae given in a previous paper (March (10)). We shall not discuss it explicitly as it

* $\chi_l'(X)_-$ is the value that $d\chi_l/dx$ takes at $x = X$ as we approach from $x < X$.

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is independent of the variational parameters and is therefore not required in their determination. The remaining part U_c can be regarded as a correction to the potential energy due to the introduction of angular terms and can be expressed in a simple form by using the orthogonality relations of the Legendre polynomials. After some manipulation the final result is

$$U_c = -\frac{3(Ze)^2}{4b}\sum_{l=1,3}\frac{1}{(2l+1)}\int_0^\infty \chi_l^2\left(\frac{\phi}{x}\right)^{\frac{1}{2}}dx + \frac{(Ze)^2X}{2b}\sum_{l=1,3}\frac{1}{(2l+1)^2}\left[\chi_l'(X)_- - \chi_l'(X)_+ - \frac{2N}{XZ}(2l+1)P_l(\cos\alpha)\right] \times\left[\chi_l'(X)_- - \chi_l'(X)_+ - \frac{(2l+1)}{X}\chi_l(X)\right], \qquad (11)$$

and the two parameters are of course implicit in the functions χ_1 and χ_3.

The evaluation of the kinetic energy is a more formidable problem for it does not seem possible to perform the integration over θ. We are left with a double integral therefore which is a function of two parameters to be determined by minimization of the total energy. Fortunately there is an approximate method which appears to be extremely useful from a computational point of view, although even this involves a good deal of labour. We again assume that the angular terms are small compared with the spherical density n_0 and expand the integrand in terms of the ratio of the angular terms to n_0. In this way the leading term simply becomes the kinetic energy due to n_0, which has again been fully discussed previously. The remainder, which we shall denote by T_c, may be expressed as shown below. We have made the substitution $z = \cos\theta$ for convenience:

$$T_c = \frac{5\pi c_k}{2b^2}\left(\frac{Z}{4\pi}\right)^{\frac{5}{3}}\left[\int_0^\infty\int_{-1}^1\left(\frac{\sum_{l=1,3}\chi_l P_l}{\phi}\right)^2\frac{\phi^{\frac{5}{2}}}{x^{\frac{1}{2}}}dz\,dx + \frac{1}{12}\int_0^\infty\int_{-1}^1\left(\frac{\sum_{l=1,3}\chi_l P_l}{\phi}\right)^4\frac{\phi^{\frac{5}{2}}}{x^{\frac{1}{2}}}dz\,dx + \frac{7}{144}\int_0^\infty\int_{-1}^1\left(\frac{\sum_{l=1,3}\chi_l P_l}{\phi}\right)^6\frac{\phi^{\frac{5}{2}}}{x^{\frac{1}{2}}}dz\,dx + \ldots\right]. \qquad (12)$$

In each term of the series given here it is possible to integrate with respect to the variable z and in this way a series involving only radial integrals can be obtained. We proceed now to investigate the usefulness of this expansion by a method of successive approximations. Let us retain only the first term in the series for T_c given in equation (12). We then carry out the minimization of $T_c + U_c$ with respect to the parameters in χ_1 and χ_3. Since the parameters appear as simple multipliers we specify them when we give the absolute values of χ_1 and χ_3 at a single point and a convenient choice is $x = X$. In this way we obtain the results shown in the first line of Table 1. At this stage we include the second term in the series for T_c and carrying through the minimization again we obtain the new values shown in the second line of Table 1. It will be seen that the inclusion of this second term has altered the parameters only by quite a small amount. Finally, if we include the third term and repeat the minimization

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then we find the values recorded in the third line of Table 1. These results leave little doubt that this method is an extremely useful one for the determination of the parameters. We have made various investigations to check the validity of the procedure, both by examining the form of higher terms and by direct numerical methods in isolated cases. These leave little doubt that the series has at least some of the properties of an asymptotic expansion and leads to essentially correct results.

Table 1

Order of approximation	$\chi_1(X)$	$\chi_3(X)$
First	0·0544	−0·0598
Second	0·0538	−0·0579
Third	0·0537	−0·0575

It is of interest to note the effect of the introduction of angular terms on the total energy. Using simply n_0 as the variational density leads to a total energy of −426·44 atomic units whereas the inclusion of f_1 and f_3 leads to a reduction in the energy of 0·35 atomic units. Such a small change makes it fairly clear that any modification of the first term n_0 in the variational density due to the inclusion of angular terms will be unimportant and we have in fact made exploratory calculations which support this view entirely.

4. *Electron density contours in plane containing molecular axis.* If we choose, to be definite, the parameters given in the third line of Table 1 then we can plot out density contours which show the way in which the spherical density n_0 is modified by the p and f terms. If we do this then we find that in a very small region of space the density n becomes very slightly negative; at the worst point to the extent of 0·001 electron per cubic Å. However, a completely unimportant change in the value of $\chi_3(X)$ for example, from −0·0575 to −0·0568, will remove this very small negative value and, from a practical point of view, such a change in the f term is completely trivial as it is not representable on density maps. (It will of course be appreciated from the values in Table 1 that strictly we have no right to expect $\chi_3(X)$ to be correct in the last decimal place due to the series method employed.) It need hardly be said, however, that whilst we believe that the density terms we have calculated will be accurate in the sense that they will be near to the correct terms in the expansion of the exact T.F. density for the present model in Legendre polynomials, in regions where complete cancellation is occurring the inclusion of higher angular terms will alter the total density appreciably. Nevertheless, except in such regions, we can expect our results to give a useful account of the distribution of electrons.

We display the results we have obtained in two ways. First of all, in Fig. 2 we show the functions ϕ, χ_1 and χ_3 which we shall use to plot density contours. These curves are sufficient to enable the density to be calculated in the present approximation in any plane. If further accuracy is ever required we shall be pleased to supply tables of χ_1 and χ_3 on request, but it seems unnecessary to give them here. Also, in Fig. 3 we have displayed our results for the electron density in a plane containing the molecular axis, as a number of interesting features are then apparent.

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First of all it can be seen that the angular terms give at least some account of the P—H bonds and if we approach sufficiently close to the two points at which the chosen plane intersects the line charge then isolated contours, which are not shown with the

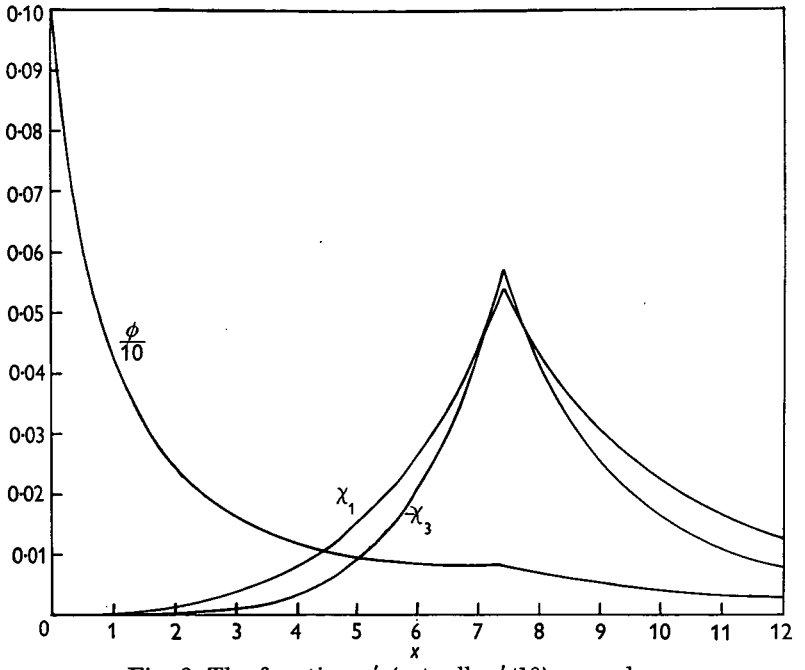


Fig. 2. The functions ϕ (actually $\phi/10$), χ_1 and χ_3.

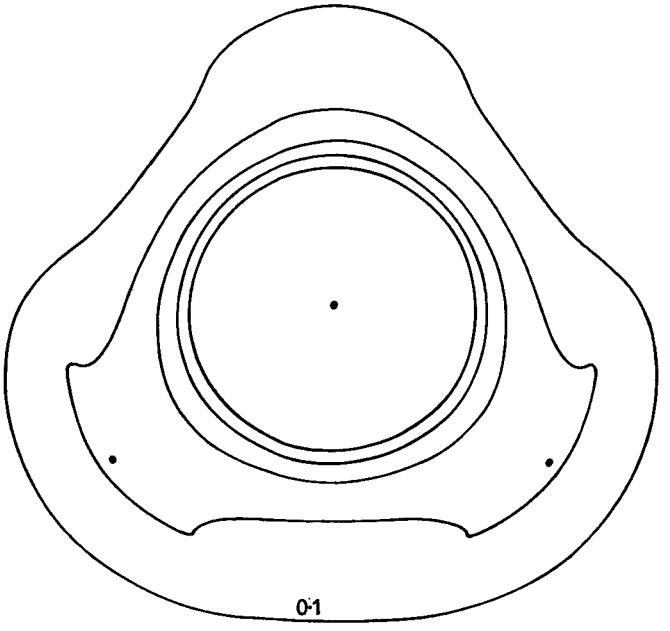


Fig. 3. Electron density contours for a plane containing the molecular axis. Interval is 0·2 electron per cubic Å. Contours corresponding to densities greater than 0·9 electron per cubic Å are not shown.

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interval we have used, appear. These represent the physical fact that there is some localization of electrons around the H nuclei although in the present model one has a kind of distorted tubular distribution around the line charge. Furthermore, if we divide the molecule into two regions by a plane containing the P nucleus and parallel to the line charge, then we can think of the additional charge which has been moved into the neighbourhood of the bonds by the introduction of angular terms as coming largely from the other half of the molecule. However, it is very interesting to observe that much more of this charge comes from around the continuations of the P—H bonds than from the molecular axis. In just this latter region conventional molecular theories predict the presence of 'lone-pair' electrons and we feel that our density contours represent this to some extent.

5. *Conclusion.* The approximate electron distribution for phosphine obtained by including p and f angular terms seems to be of considerable interest and, furthermore, leads to a potential field which should be useful in a full wave-mechanical treatment, in which one starts from central field wave functions and proceeds to refine them. Examination of X-ray scattering results for NH_3 (Banyard and March (3)) already suggests that such a method will be useful from a practical point of view and a calculation of wave functions for PH_3 using the field obtained in this work is now being planned.

Finally, it might perhaps be asked whether the present results are useful for the calculation of the dipole moment of PH_3. The answer, unfortunately, is that they are not, for Brinkman and Peperzak (5) have pointed out that any density obtained by solving the T.F. equation always leads to a zero dipole moment. This means that any non-zero value which might be found from the present work would be due to approximations employed in obtaining the density, and we have not pursued the matter.

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