remains unchanged at 74 ± 6 kcal/mole, but the absolute rate is reduced.

An alternative experimental method for evaluating the unimolecular rate constant k_2 would be a study of the pressure dependence of the gross CO_2 decomposition. However, the instrumentation used is not well suited to pressure-dependence studies since there is a distorting effect on the spectra produced by the variable pressures in the mass spectrometer, and so no such study was pursued.

The rate of Reaction (2) was less than a factor of 2 higher than previous studies of this reaction which used Ar as diluent, and the activation energy deduced was within the range observed in prior studies.[6] We conclude that the contribution of Reaction (1) to the decomposition of CO_2 in our work cannot explain the low activation energy relative to the endothermicity for Reaction (2). We are unable to offer any new explanation for this phenomenon.

The absolute values of the rate constants cited in this paper could be in error by a factor of 2, and the observed activation energies are poorly established due to the small temperature range which could be used, but the order of magnitude disparity between the absolute rates determined here and those presented in the literature[13] far exceeds the error limits of our instrumentation.

Electron Densities from Gas-Phase Electron Diffraction Intensities. I. Preliminary Considerations*

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The intensity of electrons and x rays scattered by a freely rotating molecule is determined, in the kinematic approximation, solely by the nuclear–nuclear, electron–nuclear, and electron–electron radial distribution functions of the molecule. Although these functions are one-dimensional, the latter two contain some information about the three-dimensional distribution of electrons in the molecule because the electrons are distributed relative to several nuclear reference positions and the spatial distribution of the nuclei is known. The purpose of this series of papers is to investigate the extent to which this information can be deciphered. Although published accounts have purported to show that the electron density $\rho(\mathbf{r})$ can be determined uniquely from the scattered intensity, we demonstrate that, in fact, the transformation is not unique. Nevertheless, if certain, not unreasonable, restrictions are imposed upon the form of $\rho(\mathbf{r})$, it becomes possible to make fairly detailed inferences about the three-dimensional character of the density. We propose a procedure which, although not guaranteeing a unique transformation, provides a means for deriving chemically significant knowledge about the molecular electron density from experimental gas-phase intensities.

INTRODUCTION

Although electron diffraction, x-ray diffraction, and rotational spectroscopy are the principal methods for determining molecular geometries, each measures quite different properties of molecules. Rotational spectra depend on the positions of nuclei through the moments of inertia, whereas x-ray diffraction intensities depend only on the planetary electrons. Electron diffraction offers the added advantages and complications stemming from its sensitivity to both the arrangement of nuclei and the distribution of planetary electrons. Recently, several papers have been devoted to the problem of determining electron charge distributions in addition to the more conventional determination of molecular structures by gas-phase x-ray and electron diffraction. Bartell and Gavin[1] showed that diffraction intensities are quite sensitive to effects of electron correlation in atoms as well as to one-electron densities. Tavard and co-workers[2] developed somewhat similar ideas for molecules. A few experimental measurements[3–5] have been made which indicate the feasibility of studying charge distributions with chemically useful accuracy. Particularly for molecules, the implications of

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[1] L. S. Bartell and R. M. Gavin, Jr., J. Am. Chem. Soc. **86**, 3493 (1964); J. Chem. Phys. **43**, 856 (1965); R. M. Gavin, Jr., and L. S. Bartell, *ibid.* **44**, 3687 (1966); **45**, 4700 (1966).

[2] C. Tavard, M. Rouault, and M. Roux, J. Chim. Phys. **62**, 1410 (1965); C. Tavard, Cahiers Phys. **20**, 397 (1966).

[3] R. A. Bonham and T. Iijima, J. Chem. Phys. **42**, 2612 (1965).

[4] D. A. Kohl and R. A. Bonham, J. Chem. Phys. **47**, 1634 (1967).

[5] M. Fink and J. Kessler, J. Chem. Phys. **47**, 1780 (1967).

the formalism need to be examined more fully before experimental measurements can be properly assessed. The present paper develops the mathematical background and analyzes the information contained in the observables of gas diffraction. Numerical results derived from quantum calculations and from experiment are presented in the succeeding paper to illustrate the practicality of the approach. Only electron diffraction will be considered explicitly, but the results can be readily extended to include x-ray diffraction.

THEORY

According to the first Born approximation, the total intensity of scattered electrons depends on the sine transform of:

(a) the nuclear charge distribution, i.e., the positions of the nuclei in the scatterer,

(b) the electron density $\rho(\mathbf{r})$ relative to the nuclear framework, and

(c) the electron–electron function $\rho_c(\mathbf{r})$ describing the density of electrons relative to the other electrons,[1] as specified below.

For simplicity, we shall consider only a scattered intensity which has been averaged over all orientations of the scatterer and shall neglect any inadequacies introduced by the adoption of the Born approximation. Furthermore, we shall limit our initial treatment to the case of a homonuclear diatomic molecule with nuclear charges of Z, containing $2Z$ electrons. If ψ is the total electronic wavefunction for the molecule, it follows that

$$\rho(\mathbf{r}) = \sum_{i=1}^{2Z} \int d\tau_1 \cdots d\tau_{2Z} \psi^* \psi \delta(\mathbf{r}-\mathbf{r}_i) \qquad (1a)$$

and

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{2Z} \sum_{\substack{j=1 \\ i \neq j}}^{2Z} \int d\tau_1 \cdots d\tau_{2Z} \psi^* \psi \delta(\mathbf{r}-\mathbf{r}_i+\mathbf{r}_j), \quad (1b)$$

where $d\tau_i$ is the volume element for integration over both space and spin variables for the ith electron. The functions $\rho(\mathbf{r})$ and $\rho_c(\mathbf{r})$ are the diagonal components of the first- and second-order density matrices, respectively. If one of the nuclei is chosen as the origin of the coordinate system and if the position of the other nucleus is given by the vector $\mathbf{r}_{AB}$, the total scattered intensity for electrons $I_{tot}(s)$[6] can be expressed as

$$s^4 I_{tot}(s) = 2Z^2 \langle 1+j_0(sr_{AB}) \rangle_{vib} + 2Z$$

$$-4Z \left\langle \int d\mathbf{r} j_0(sr)[\rho(\mathbf{r})+\rho(\mathbf{r}+\mathbf{r}_{AB})] \right\rangle_{vib}$$

$$+ \left\langle \int d\mathbf{r} j_0(sr)\rho_c(\mathbf{r}) \right\rangle_{vib}, \quad (2)$$

where s is the scattering variable, $(4\pi/\lambda) \sin(\phi/2)$, ϕ the scattering angle, λ the electron wavelength, $\langle\ \rangle_{vib}$ denotes vibrational averaging, and $j_0(x)$ is the zeroth-order spherical Bessel function. For a simpler notation the symbol for vibrational averaging will be omitted from the equations to follow. Since the prime concern is in the electronic contributions to the scattered intensity, it is convenient, following Bonham,[7] to introduce the notation

$$\sigma_{tot}(s) = s^4 I_{tot}(s) - 2Z^2[1+j_0(sr_{AB})] - 2Z \qquad (3a)$$

$$= -4Z \int d\mathbf{r} j_0(sr)[\rho(\mathbf{r})+\rho(\mathbf{r}+\mathbf{r}_{AB})]$$

$$+ \int d\mathbf{r} j_0(sr)\rho_c(\mathbf{r}). \quad (3b)$$

In addition, we shall subdivide

$$\sigma_{tot}(s) = \sigma_{ne}(s) + \sigma_{ee}(s) \qquad (4)$$

into the components $\sigma_{ne}(s)$ and $\sigma_{ee}(s)$ which correspond to the terms of Eq. (3b) depending on the electron–nuclear $\rho(\mathbf{r})$ and electron–electron $\rho_c(\mathbf{r})$ contributions, respectively. The distinction between the components of Eq. (4) may be made from the experimental observations as well as from theoretical definition.[1,2,7] It is clear from the dependence of $\sigma_{tot}(s)$ on the density functions that the integration over angular variables can be done immediately, with the result

$$\sigma_{tot}(s) = -4Z \int_0^\infty dr j_0(sr)D(r) + \int_0^\infty dr j_0(sr)P(r), \quad (5)$$

where

$$D(r) = r^2 \int d\Omega[\rho(\mathbf{r})+\rho(\mathbf{r}+\mathbf{r}_{AB})]$$

and

$$P(r) = r^2 \int d\Omega \rho_c(\mathbf{r})$$

represent the (spherically averaged) radial distribution functions of electrons relative to the nuclei and relative to other electrons, respectively.

The distributions $D(r)$ and $P(r)$ can be deduced at once from the Fourier sine transforms of $s\sigma_{ne}(s)$ and $s\sigma_{ee}(s)$. Since $D(r)$ and $P(r)$ are one-dimensional functions, it is not obvious that $\sigma_{tot}(s)$ and, hence, the total scattered intensity depend upon the three-dimensional character of the charge densities. Some three-dimensional information must survive, however, because of the fact that the electron distribution is referenced to several nuclei, the three-dimensional arrangement of which is known. Indeed, Tavard, Rouault, and Roux[2] have proposed a method for obtaining a three-dimensional density function from a knowledge of $\sigma_{ne}(s)$ alone, arguing that a unique

[6] The symbol $I_{tot}(s)$ designates an intensity adjusted by a constant scale factor to yield the Born approximation asymptotic value of $2(Z^2+Z)$ for $s^4 I_{tot}(s)$.

[7] R. A. Bonham, J. Phys. Chem. 71, 856 (1967).

solution can be established. Since $\sigma_{ne}(s)$ can, at least in principle, be determined experimentally,[2,7] the proposal of Tavard *et al.* implies that it is possible to obtain $\rho(\mathbf{r})$ from experimental gas-phase intensities.

The method described in Ref. 2 for transforming $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$ is an iterative procedure for obtaining numerical values of the electron density point-by-point. The apparent success of Tavard's treatment notwithstanding, we have been able to demonstrate that a not inconsiderable arbitrariness still remains in the transformation from $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$ if it is only required that a finite number of derivatives of $\rho(\mathbf{r})$ be continuous (see Appendix). For this reason, no procedure leading to a strictly numerical representation of electron density can escape the problem of non-uniqueness of solution. Nevertheless, even if it is impossible to obtain a unique electron density directly and unambiguously from scattered intensities, one may reasonably hope that useful results can be obtained if certain constraints are imposed. The simplest scheme for accomplishing this is to adopt an analytical representation for $\rho(\mathbf{r})$.

We propose an expansion about each nucleus of the form

$$\sum_{n=0}^{\infty} \sum_{l=-n}^{n} \rho_n(r) Y_n^l(\theta, \phi), \qquad (6)$$

where $Y_n^l(\theta, \phi)$ are the spherical harmonics. For a homonuclear diatomic molecule with axial symmetry, Eq. (6) reduces to

$$\rho(r, \theta) = \sum_{n=0}^{\infty} [\rho_n(r) P_n(\cos\theta) + \rho_n(r') P_n(\cos\theta')], \quad (7)$$

where

$$r' = (r^2 + r_{AB}^2 - 2r r_{AB} \cos\theta)^{1/2},$$

$$r = (r'^2 + r_{AB} - 2r' r_{AB} \cos\theta')^{1/2},$$

and $P_n(x)$ is the Legendre polynomial of degree n. The corresponding expression for $\sigma_{ne}(s)$ is given by

$$\sigma_{ne}(s) = -16\pi Z \sum_n g_n(s),$$

where

$$g_n(s) = [\delta_{n0} + j_n(s r_{AB})] \int_0^{\infty} dr r^2 j_n(sr) \rho_n(r) \qquad (8)$$

and $j_n(x)$ is the spherical Bessel function of order n.

Even if $\rho(r, \theta)$ were known exactly, the subdivision into expansions about the A and B centers is not unique, in consequence of the overflexibility of the form of Eq. (7). Accordingly, neither the $\rho_n(r)$ nor the $g_n(s)$ are unambiguously defined, let alone derivable from experiment. It turns out, however, that a very natural choice of the $\rho_n(r)$ can be made. When the $\rho_n(r)$ are established, the shapes of the $g_n(s)$ are fixed. Unfortunately, the converse is not true, illustrating in yet another way the nonuniqueness of the $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$

transformation. That is, any particular scattering component, $g_n(s)$, corresponding to an nth-order spatial component $\rho_n(r)$, can also be expressed in s space as $g_0^n(s)$, a component which would arise from the bounded, zeroth-order spatial component

$$\rho_0^n(r) = \frac{2}{\pi} \int_0^{\infty} ds \frac{s^2 j_0(sr) g_n(s)}{[1 + j_0(s r_{AB})]}. \qquad (9)$$

Therefore, the entire function $\sigma_{ne}(s)$ can be expressed in terms of zeroth-order terms corresponding to the overlapping of noninteracting atoms, to each of which is ascribed a spherical density distribution. This new molecular density so constructed possesses a radial distribution function $D(r)$ identical to the original one even though the new density may be markedly different from the original. A similar representation of an nth-order component $g_n(s)$ in terms of an lth-order component $\rho_l'(r)$ with $0 \neq l \neq n$ cannot be made arbitrarily, due to the distinctly different nodal patterns of $j_l(x)$ and $j_n(x)$. The spherical atom, zeroth-order component "solution" of the transformation from $\sigma_{ne}(s)$ to $\rho(r)$, in which all $\rho_n(r)$ are mapped into $\rho_0^n(r)$ functions, has a marked oscillatory behavior. Whether this "solution" can be ruled out on physical grounds is investigated in the following paper. Obviously, at some point intermediate between the "true" and the extreme $\rho_0^n(r)$ solutions, physical arguments, blunted by experimental errors, would lose their force.

The problem of interpreting $\sigma_{ne}(s)$ on the basis of the analytical expressions (6)–(8) is that the expressions are infinitely flexible in representing (well-behaved) densities. If arbitrariness is to be removed from the actual $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$ transformation, it can only be done at the cost of greatly reducing the flexibility of the functions chosen to represent $\rho(\mathbf{r})$. The simplest procedure for doing this, perhaps, is to focus attention upon the Roux function

$$\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{atom}(\mathbf{r}), \qquad (10)$$

the difference between the correct density $\rho(\mathbf{r})$ and $\rho_{atom}(\mathbf{r})$, the density corresponding to a superposition of (noninteracting) atomic electron densities. The Roux function strikingly reflects the effects of bond formation. It is also extremely sensitive to the accuracy of $\rho(\mathbf{r})$. Approximate wavefunctions which correspond to nearly the same total energy sometimes yield quite different Roux functions,[8] especially if somewhat different basis sets are used in the calculations. We shall assume that accurate densities for free atoms are known. If, in addition, it is assumed that $\Delta \rho(\mathbf{r})$ is not large and that it can be expressed by a limited number of analytical terms, it is possible to derive a result for $\Delta \rho(\mathbf{r})$ and, hence, for $\rho(\mathbf{r})$ from experiment.

[8] C. W. Kern and M. Karplus, J. Chem. Phys. 40, 1374 (1964) See Figs. 6–10 for some samples.

Consider the difference $\Delta\sigma_{ne}(s)$ between $\sigma_{ne}(s)$ calculated from the correct electron density $\rho(\mathbf{r})$ and $\sigma_{ne}{}^0(s)$ calculated from some reference electron density $\rho^0(\mathbf{r})$. The equation defining $\Delta\sigma_{ne}(s)$ is then

$$\Delta\sigma_{ne}(s) = \sigma_{ne}(s) - \sigma_{ne}{}^0(s)$$

$$= -4Z \int \mathbf{dr} j_0(sr) [\rho(\mathbf{r}) - \rho^0(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{r}_{AB})$$

$$-\rho^0(\mathbf{r} + \mathbf{r}_{AB})]. \quad (11)$$

Although the choice of $\rho^0(\mathbf{r})$ is arbitrary, for practical purposes, it is probably best to let $\rho^0(\mathbf{r})$ be given by the superposition of atomic electron densities. The equation to be solved is then

$$\Delta\sigma_{ne}(s) = -4Z \int \mathbf{dr} j_0(sr) [\Delta\rho(\mathbf{r}) + \Delta\rho(\mathbf{r} + \mathbf{r}_{AB})], \quad (12)$$

where $\Delta\rho(\mathbf{r})$ is the Roux function. It is plausible to adopt the functional form

$$\Delta\rho(\mathbf{r}) = \Delta\rho(r, \theta) = \sum_n \sum_{k \geq n-1} a_{nk} [P_n(\cos\theta) r^k$$

$$\times \exp(-\lambda_{nk} r) + P_n(\cos\theta') (r')^k \exp(-\lambda_{nk} r')], \quad (13)$$

where a_{nk} and λ_{nk} are adjustable parameters. Independent of the choice of parameters, this representation has the required symmetry properties. The function $\Delta\sigma_{ne}(s)$ can be expressed analytically as

$$\Delta\sigma_{ne}(s) = -16\pi Z \sum_n \sum_{k \geq n-1} a_{nk} n! 2^n [\delta_{n0} + s^n j_n(sr_{AB})]$$

$$\times (-\partial/\partial\lambda_{nk})^{k-n+1} (\lambda_{nk}{}^2 + s^2)^{-n-1}. \quad (14)$$

If a sufficiently limited number of terms is selected, the adjustable parameters can be determined empirically by a least-squares fitting of the observed $\Delta\sigma_{ne}(s)$ function by its representation, Eq. (14). The insertion of these parameters into Eq. (13) yields a reasonable estimate of $\Delta\rho(\mathbf{r})$ and, hence, of $\rho(\mathbf{r})$. Guidelines for the number of terms to be retained and for the most effective n and k are presented in the following paper.

There are two definite constraints on the Roux function. Since the volume integral over all space of $\rho(\mathbf{r})$ is equal to the total number of electrons, the volume integral of $\Delta\rho(\mathbf{r})$ must be equal to zero. Only the terms in Eq. (13) with $n=0$ make nonzero contributions to this normalization condition. For these terms, obvious restrictions on the a_{0k} and λ_{0k} are required. Also, while the Roux function may be positive or negative, in negative regions the nonnegative requirement for the total electron density requires that $|\Delta\rho(\mathbf{r})| \leq \rho^0(\mathbf{r})$. Because of the relative magnitudes of the two functions, this constraint is only effective at large distances from the nuclei.

CONCLUSIONS

We have established, contrary to some published conjectures, that there are definite limitations on the extent of three-dimensional information surviving in the intensity scattered by freely rotating molecules. Nevertheless, because gas-phase intensity measurements are free from certain difficulties inherent in measurements on crystals, and because of the great potential value of experimental information on molecular electron density functions, it is profitable to pursue the problem. Of particular interest are details of the Roux function $\Delta\rho(\mathbf{r})$, showing the effect of bonding on planetary electrons and $\Delta\sigma_{ne}(s)$, the observable manifestation of one-electron bonding effects on the scattered intensity. We have proposed a scheme for deriving some properties of $\Delta\rho(\mathbf{r})$ from $\Delta\sigma_{ne}(s)$. Calculations of $\Delta\sigma_{ne}(s)$ based on the best current quantum calculations of $\Delta\rho(\mathbf{r})$ are encouraging in their indications that gas diffraction can provide significant, if not complete, knowledge about bonding effects in molecules. These calculations are presented in the following paper.

APPENDIX: THE NONUNIQUENESS OF THE TRANSFORMATION FROM $\sigma_{ne}(s)$ TO $\rho(\mathbf{r})$

For a homonuclear diatomic molecule, the observable $\sigma_{ne}(s)$ is related to the electron density $\rho(\mathbf{r})$ by the integral equation

$$\sigma_{ne}(s) = -4Z \int \mathbf{dr} j_0(sr) [\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{r}_{AB})]. \quad (A1)$$

Since $\rho(\mathbf{r}) = \rho(r, \theta)$ is the electron density for the molecule, the angular dependence is not arbitrary because the electron density must be independent of the choice of the origin of the coordinate system. In other words, the following relation must hold:

$$\rho(r, \theta) = \rho(r', \theta'), \quad (A2)$$

where r, θ, r', and θ' are defined in Fig. 1. Using Eqs. (A1) and (A2), Tavard, Rouault, and Roux devised an iterative numerical procedure for obtaining $\rho(r, \theta)$
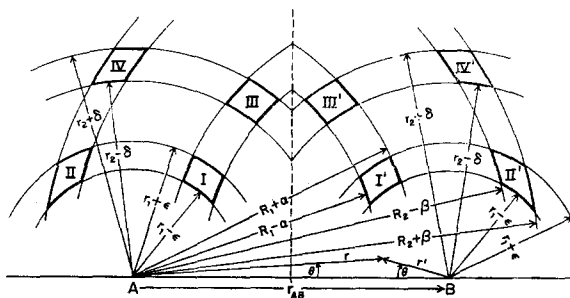

FIG. 1. Geometrical construction for the "four-area" proof of the nonuniqueness of the transformation from $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$.

from $\sigma_{ne}(s)$. However, if $\rho'(r, \theta)$ is a solution of Eq. (A1), it can be shown that there exists a function $\rho'(r, \theta) + \rho''(r, \theta)$ which is also a solution. In Fig. 1 a coordinate system and eight regions in space are defined. Since a homonuclear diatomic molecule has a plane of symmetry perpendicular to the internuclear axis, only four of these regions are independent as each region has a mirror image. Each region is bounded by two arcs whose center is nucleus A and two arcs whose center is nucleus B. With the well-behaved but otherwise arbitrary functions $f(r)$ and $g(r)$, $\rho''(r, \theta)$ will be

defined in each of the regions as

$$\rho_i''(r, \theta) = A_i \begin{cases} f(r)g(r'), & \text{where } i=1, 2, 3, \text{ or } 4, \\ f(r')g(r), & \text{where } i=1', 2', 3', \text{ or } 4', \\ 0 & \text{elsewhere,} \end{cases} \quad \text{(A3)}$$

where r_{AB} is the distance between the nuclei and A_i is a constant. To preserve symmetry we must choose $A_1 = A_{1'}$, $A_2 = A_{2'}$, etc. The contribution to $\sigma_{ne}(s)$ from $\rho_1''(r, \theta)$ and $\rho_{1'}''(r, \theta)$ is

$$A_1 \int_{r_1-\epsilon}^{r_1+\epsilon} dr\, r^2 j_0(sr) f(r) \int_{\theta(R_1-\alpha)}^{\theta(R_1+\alpha)} d\theta\, \sin\theta\, g(r') + A_1 \int_{R_1-\alpha}^{R_1+\alpha} dr\, r^2 j_0(sr) g(r) \int_{\theta(r_1-\epsilon)}^{\theta(r_1+\epsilon)} d\theta\, \sin\theta\, f(r'). \quad \text{(A4)}$$

After transforming the integration over $d\theta$ into an integration over x, where $x^2 = (r^2 + r_{AB}^2 - 2rr_{AB}\cos\theta)$, the result

$$A_1 \int_{r_1-\epsilon}^{r_1+\epsilon} dr\, r^2 j_0(sr) f(r) \int_{R_1-\alpha}^{R_1+\alpha} dx\, x\, g(x) + A_1 \int_{R_1-\alpha}^{R_1+\alpha} dr\, r^2 j_0(sr) g(r) \int_{r_1-\epsilon}^{r_1+\epsilon} dx\, x\, f(x) \quad \text{(A5)}$$

is obtained. If the contribution from each region is treated in an analogous manner and like terms are grouped, the total contribution from $\rho''(r, \theta)$ is given by

$$\left[A_1 \int_{R_1-\alpha}^{R_1+\alpha} dx\, x\, g(x) + A_2 \int_{R_2-\beta}^{R_2+\beta} dx\, x\, g(x) \right] \int_{r_1-\epsilon}^{r_1+\epsilon} dr\, r^2 j_0(sr) f(r)$$

$$+ \left[A_3 \int_{R_1-\alpha}^{R_1+\alpha} dx\, x\, g(x) + A_4 \int_{R_2-\beta}^{R_2+\beta} dx\, x\, g(x) \right] \int_{r_2-\delta}^{r_2+\delta} dr\, r^2 j_0(sr) f(r)$$

$$+ \left[A_1 \int_{r_1-\epsilon}^{r_1+\epsilon} dx\, x\, f(x) + A_3 \int_{r_2-\delta}^{r_2+\delta} dx\, x\, f(x) \right] \int_{R_1-\alpha}^{R_1+\alpha} dr\, r^2 j_0(sr) g(r)$$

$$+ \left[A_2 \int_{r_1-\epsilon}^{r_1+\epsilon} dx\, x\, f(x) + A_4 \int_{r_2-\delta}^{r_2+\delta} dx\, x\, f(x) \right] \int_{R_2-\beta}^{R_2+\beta} dr\, r^2 j_0(sr) g(r). \quad \text{(A6)}$$

Clearly, the contributions to $\sigma_{ne}(s)$ can be made identically zero by choosing

$$A_2 = -A_1 \int_{R_1-\alpha}^{R_1+\alpha} dx\, x\, g(x) \Big/ \int_{R_2-\beta}^{R_2+\beta} dx\, x\, g(x),$$

$$A_3 = -A_1 \int_{r_1-\epsilon}^{r_1+\epsilon} dx\, x\, f(x) \Big/ \int_{r_2-\delta}^{r_2+\delta} dx\, x\, f(x), \quad \text{(A7)}$$

and setting $A_1/A_2 = A_3/A_4$. Since $f(r)$ and $g(r)$ are arbitrary functions, they can be chosen such that $\rho''(r, \theta)$ goes to zero at the boundaries of the eight regions and therefore $\rho'(r, \theta) + \rho''(r, \theta)$ will be a continuous function. If further restrictions are placed on $\rho''(r, \theta)$, the function $\rho'(r, \theta) + \rho''(r, \theta)$ can be constructed to have a number of continuous derivatives. Moreover, once the above "four-area" key to constructing alternative solutions has been found, even more flexible alternative solutions are easy to visualize.

Arbitrary linear combinations of "four-area" solutions are also solutions. Consequently, among other things, the boundaries of the four regions can be relaxed from their rigid "quasiparallelogram" shapes to smoothly rounded shapes.

Tavard's conjectures[2] that the transformation from $\sigma_{ne}(s)$ to $\rho(\mathbf{r})$ is unique was based partly upon his recognition that a reapportionment of density among three regions could not leave $\sigma_{ne}(s)$ invariant. The above construction proves that a reapportionment among four or more regions can leave $\sigma_{ne}(s)$ invariant. A yet different remapping of density which leaves $\sigma_{ne}(s)$ unchanged is that embodied in Eq. (9) of the text. Obviously, neither type of remapping is completely arbitrary if physically significant, nonnegative densities are to result. Nevertheless, if the only condition on $\rho(r, \theta)$ is that it be positive and possess a finite number of continuous derivatives, a rather considerable arbitrariness has been found to exist in its derivation from gas-diffraction information.