

## Numerical Applications of a Quantum Model for the Coherent Diffraction Experiment

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(Received 12 January 1981; accepted 23 July 1981)

### Abstract

The coherent X-ray diffraction experiment may be used to determine an electron density matrix for a crystal. Equations are displayed whose purpose is to convert measured scattering intensities (or structure factors) into a density matrix corresponding to a single determinant of molecular orbitals. With H and H<sub>2</sub> as model systems it is shown that the equations may be solved and that the solutions are physically meaningful. The results are compared to those obtained by ordinary least-squares refinement.

### Introduction

The structure factors derived from the coherent X-ray diffraction experiment are related to the electronic density distribution,  $\rho(\mathbf{r})$ , of the unit cell in the following way:

$$F(\mathbf{k}) = \int \rho(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (1)$$

It is the intensities

$$I(\mathbf{k}) = F(\mathbf{k}) F^*(\mathbf{k}) \quad (2)$$

that are observed in this experiment at discrete values of the scattering vector,  $\mathbf{k}$ . It is assumed here that thermal effects and other experimental conditions which modify the ideal intensities can be accounted for independently of the form of the electron density. It is also assumed that the nuclear positions have been previously determined. To emphasize the quantum mechanical nature of the electron density and the closely related function  $\rho(\mathbf{r}, \mathbf{r}')$ , the one-body reduced density matrix, we write the following definitions:

$$\rho(\mathbf{r}, \mathbf{r}') = N \int \Psi(\mathbf{r}_1, \mathbf{s}_1, \mathbf{x}_2 \dots \mathbf{x}_n) \Psi^*(\mathbf{r}'_1, \mathbf{s}'_1, \mathbf{x}_2 \dots \mathbf{x}_n) \times dx_2 \dots dx_n ds_1 \quad (3a)$$

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}), \quad (3b)$$

where  $\mathbf{x}_i$  denotes both space coordinates  $\mathbf{r}_i$  and spin coordinates  $\mathbf{s}_i$ . The wave functions in (3a) depend parametrically upon nuclear coordinates. Hence

measured X-ray intensities and structure factors will be ensemble average properties (Clinton, Frishberg, Massa & Oldfield, 1981). The one-body reduced density matrix is obtained by integrating the square of the wave function over the coordinates of all particles but one, over the spin coordinate of the remaining particle, and multiplying the result by the number of electrons. Since  $\Psi$  is antisymmetric with respect to the interchange of the coordinates of any pair of electrons,  $\rho(\mathbf{r}, \mathbf{r}')$  can be used to calculate the expectation value of any one-body property. The diagonal 'elements' of this matrix,  $\rho(\mathbf{r}, \mathbf{r})$ , measure the probability of finding an electron at position  $\mathbf{r}$ . The requirements imposed by quantum mechanics upon the wave function will restrict the class of functions which are acceptable densities. Although the practice of taking  $\rho(\mathbf{r})$  to be a sum of spherical atomic densities has been very successful in determining crystal structures, it is well known (Coppens, 1975*a,b*) that X-ray diffraction data can be accurate enough to obtain features of the electron density which go beyond the isolated-atom approximation. Therefore, it is expected that (3) will become more important as more detailed information is sought from the data. That is to say that any density function should be related to an antisymmetric  $N$ -body wavefunction *via* (3). The complete set of necessary and sufficient conditions on the density is not presently agreed upon, but the conditions on  $\rho(\mathbf{r}, \mathbf{r}')$  are well known. All eigenvalues of the one-body reduced density matrix must be bounded by 0 and 1.

$$\int \rho(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}') d\mathbf{r}' = \varepsilon_i \varphi_i(\mathbf{r}) \quad (4)$$

$$0 \leq \varepsilon_i \leq 1 \quad \text{for all } i.$$

It is clear from (3) that any density which is the diagonal part of an  $N$ -representable density matrix will be a valid density.

Expansion of the density in atomic orbital products is a model used by several workers in this field (Stewart, 1969; Coppens, Willoughby & Csonka, 1971; Matthews, Stucky & Coppens, 1972). It is flexible enough to describe accurately the density of a unit cell. Overlap products simulate bonding and

polarization orbitals can account for lone-pair electrons. If the weighting coefficients of the atomic-orbital products are to be interpreted as population coefficients and compared to theoretical wavefunction calculations, it is imperative that the restrictions imposed by quantum mechanics, specifically equations (4), be adhered to. We have already proposed (Clinton & Massa, 1972; Clinton, Frishberg, Massa & Oldfield, 1973, 1981) that these restrictions be accounted for by seeking an idempotent density matrix that most closely fits the X-ray diffraction data. Idempotency of  $\rho(\mathbf{r}, \mathbf{r}')$ , *i.e.*

$$\int \rho(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' = \rho(\mathbf{r}, \mathbf{r}''), \quad (5)$$

ensures that it is  $N$ -representable by a single determinant of normalized and mutually orthogonalized molecular orbitals (Massa & Clinton, 1972). If one chooses the molecular orbitals such that the expectation value of the energy is minimized, the Hartree-Fock solution would result. However, here we do not use the energy as a criterion for determining the molecular orbitals but rather use data from the X-ray experiment.

Inherent in the single-determinant approximation is the assumption that the electrons do not interact explicitly, but that the effect of interactions can be accounted for by averaging. It is expected that the error introduced by this assumption should not affect the ability of an idempotent density to interpret diffraction data which are accurate to about 1%.

In this paper we present evidence that the algorithm proposed by Clinton *et al.* (1981) is numerically viable and leads to reasonable results. This is the first time a least-absolute-value constraint has been tested in the idempotent  $P$  equations. In the next section we give a brief review of the formalism and in the following section we report some numerical results of applying it to the one- and two-electron systems of the hydrogen atom and molecule. Although these systems are simple compared to those encountered by the experimentalist, they are still of value in providing numerical experiments with which to explore our method and with which to get an initial assessment of the importance of  $N$ -representability. Such numerical experiments are also valuable in allowing one to control precisely the magnitude of the effects due to temperature and to the scale factor. Our method for imposing  $N$ -representability on the density in the context of structure factor constraints is untried, and so it is natural to begin by applying it to systems that are as simple as possible but have the main features of more complicated systems so that future generalization is possible.

The results presented here clearly show that our method can be used to determine the elements of the density matrix. The imposition of quantum mechanical requirements allows us to fix the off-diagonal 'elements', *i.e.*  $\rho(\mathbf{r}, \mathbf{r}')$ , from density-dependent data alone.

It is also shown that an ordinary least-squares fit does not allow this to be done, and that completely ignoring  $N$ -representability constraints may result in non-physical electron densities. Fixing the density matrix enables us to compare our experimental results with those obtained by strictly theoretical investigations. We expect the comparison with theory to become more and more important as experimental accuracy increases and as crystallographers seek the maximum amount of information from their efforts.

### Formalism

In an atomic orbital basis, the density matrix  $\rho(\mathbf{r}, \mathbf{r}')$  is represented by a matrix  $\mathbf{P}$  according to

$$\rho(\mathbf{r}, \mathbf{r}') = \text{tr } \mathbf{P} \Psi(\mathbf{r}) \Psi^+(\mathbf{r}'), \quad (6)$$

where  $\Psi$  is a column matrix of the basis vectors. Condition (5) translates into the matrix equation for  $\mathbf{P}$ :

$$\mathbf{P} \mathbf{S} \mathbf{P} = \mathbf{P}, \quad (7)$$

where  $\mathbf{S}$  is the overlap matrix of the basis. In addition to being idempotent, the density matrix must be Hermitian and normalized to the number of molecular orbitals  $N$ :

$$\mathbf{P}^+ = \mathbf{P} \quad (8)$$

$$\text{tr } \mathbf{P} \mathbf{S} = N. \quad (9)$$

To determine the elements of  $\mathbf{P}$ , the following least-absolute-value constraint is imposed:

$$\sum_{\mathbf{k}} w_{\mathbf{k}} |\text{tr } \mathbf{P} \mathbf{O}(\mathbf{k}) - \langle O(\mathbf{k}) \rangle| = \varepsilon. \quad (10)$$

The scalar  $\varepsilon$  is made as small as possible to ensure the best fit to a set of data. The data points  $\langle O(\mathbf{k}) \rangle$ , which are weighted by  $w_{\mathbf{k}}$ , are expectation values of operators having matrix representatives  $\mathbf{O}(\mathbf{k})$ . If X-ray structure factors are used as data points, the operator matrices will be the Fourier transforms of all basis orbital products, evaluated at the various values of the scattering vector  $\mathbf{k}$ :

$$\mathbf{O}_{ij}(\mathbf{k}) = \int \Psi_i(\mathbf{r}) \Psi_j^*(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \equiv \mathbf{f}_{ij}(\mathbf{k}). \quad (11)$$

This matrix need not be Hermitian. However, if intensities are used as data points, the operator matrices are taken to be

$$\mathbf{O}_{ij}(\mathbf{k}) = \mathbf{f}_{ij}(\mathbf{k}) \text{tr } \mathbf{P} \mathbf{f}^+(\mathbf{k}) + \mathbf{f}_{ij}^+(\mathbf{k}) \text{tr } \mathbf{P} \mathbf{f}(\mathbf{k}) \quad (12)$$

which are of necessity Hermitian. In this case the operator is a function of the current  $\mathbf{P}$  matrix and must be updated on every iteration; at solution it will not change. The motivation for choosing (10), rather than the more conventional least-squares functional, is that it leads to a linear equation for the Lagrangian multipliers whereas the latter does not.

Idempotency is achieved by reducing  $\text{tr}(\mathbf{PSP} - \mathbf{P})^2$  to zero and using the Lagrangian multiplier technique to enforce (9) and (10). (Hermiticity will be preserved throughout the iterations as long as the initial guess is Hermitian.) We arrive at the following iterative equation for  $\mathbf{P}$ :

$$\mathbf{P}_{n+1} = \mathcal{P}_n + \lambda_1 \mathbf{S} + \lambda_2 \mathbf{G} \quad (13)$$

with

$$\mathcal{P}_n = \mathbf{P}_n \mathbf{S} \mathbf{P}_n + \mathbf{P}_n^2 \mathbf{S} + \mathbf{S} \mathbf{P}_n^2 - \mathbf{P}_n \mathbf{S} \mathbf{P}_n^2 \mathbf{S} - \mathbf{S} \mathbf{P}_n^2 \mathbf{S} \mathbf{P}_n \quad (14)$$

and

$$\mathbf{G} = \sum_{\mathbf{k}_+} w_{\mathbf{k}_+} \mathbf{O}(\mathbf{k}_+) - \sum_{\mathbf{k}_-} w_{\mathbf{k}_-} \mathbf{O}(\mathbf{k}_-). \quad (15)$$

A data point is in the  $\mathbf{k}_+$  group if  $[\text{tr } \mathbf{PO}(\mathbf{k}) - \langle \mathbf{O}(\mathbf{k}) \rangle] \geq 0$ , otherwise it is in the  $\mathbf{k}_-$  group. Alternatively, one can define

$$\mathbf{R} \equiv \mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2} \quad (16)$$

and thus the iterative equation for  $\mathbf{R}$  becomes

$$\mathbf{R}_{n+1} = 3\mathbf{R}_n^2 - 2\mathbf{R}_n^3 + \lambda_1 \mathbf{1} + \lambda_2 \mathbf{S}^{-1/2} \mathbf{G} \mathbf{S}^{-1/2}. \quad (17)$$

The Lagrangian multipliers are determined on every iteration by

$$\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} = \begin{pmatrix} \text{tr } \mathbf{S} \mathbf{S} \\ \text{tr } \mathbf{G} \mathbf{S} \end{pmatrix} \begin{pmatrix} \text{tr } \mathbf{S} \mathbf{G} \\ \text{tr } \mathbf{G} \mathbf{G} \end{pmatrix}^{-1} \\ \times \begin{pmatrix} N - \text{tr } \mathcal{P} \mathbf{S} \\ \varepsilon + \sum_{\mathbf{k}_+} \langle \mathbf{O}(\mathbf{k}_+) \rangle - \sum_{\mathbf{k}_-} \langle \mathbf{O}(\mathbf{k}_-) \rangle - \text{tr } \mathcal{P} \mathbf{G} \end{pmatrix}. \quad (18)$$

When an idempotent  $\mathbf{P}$  is found which satisfies (10),  $\varepsilon$  is decremented and the process repeated until the smallest value of  $\varepsilon$  consistent with an idempotent  $\mathbf{P}$  is found.

The application of this formalism is simple and straightforward. First, it requires the selection of an appropriate basis for the symmetry of the unit cell. Guidelines for such a choice have been extensively studied within the context of variational calculations of quantum chemistry, and the results should be generally valid for this type of analysis also. Then the Fourier transforms of all orbital products must be evaluated; this is facilitated by the use of Gaussian functions since there will ordinarily be many two-center integrals. Finally, iteration with (13) or (17) involves matrix multiplications and additions, and the inversion of the simple  $2 \times 2$  dimensional matrix in (18).

We realize that one of the major obstacles which has discouraged the use of atomic basis orbitals in the refinement of X-ray data is the large number of parameters that must be determined. Since the number of data points available is limited by the diffraction experiment, the crystals amenable to this type of treatment are those with unit cells characterized by

relatively few parameters and many observable reflections. The number of parameters that must be determined in a normalized, symmetric matrix of dimension  $m$  is  $(m^2 + m - 2)/2$ . But, in an idempotent matrix, all these elements are not independent and the number of free parameters is greatly reduced. In fact, the increase in parameters is linearly dependent on the basis size and not quadratically as in most other formalisms used in this type of analysis. The number of independent parameters in an idempotent matrix is  $(Nm - N^2)$  where  $N$  is the number of molecular orbitals (one-half the number of electrons for a closed-shell system). When these many constraints are imposed, the elements of  $\mathbf{P}$  should be uniquely determined. However, we are using only one constraint, (10), regardless of the size of the basis. With ordinary constraints, an underconstrained problem will have an infinite number of solutions. But a least-absolute-value constraint, such as (10), forces the  $\mathbf{P}$  matrix to fit at many points in reciprocal space and is a much stronger requirement than one ordinary constraint.

In the next section we report some simple numerical results which illustrate the general convergence properties of the proposed algorithm. These examples deal with the questions of initial guess dependence, resulting from the under-constrained nature of the problem as discussed above, and multiple solutions resulting from the essentially quadratic nature of the basic equations. We present unrestricted least-squares solutions for comparison when possible, and point out some advantages of imposing  $N$ -representability.

### Numerical examples

*A. Hydrogen atom.* The data used here are the real structure factors given by Stewart, Davidson & Simpson (1965) for a spherical hydrogen atom in a hydrogen molecule. They used eleven spherical STO's to fit the density of the essentially exact Kolos-Roothaan  $\text{H}_2$  wavefunction. Forty-five pieces of data are included in the set and range from  $\sin \theta/2 = 0.0215$  to  $1.7176 \text{ \AA}^{-1}$ . The basis set we employ consists of  $s$ -type hydrogenic functions with a variable exponent  $\zeta$ . We point out that the exact solution for this system is idempotent since there is only one electron.

Table 1 illustrates that initial guess dependence does not appear to be a problem here. Four basis functions are used (with  $\zeta = 1.00$  and all weighting factors unity) so that the number of free parameters in  $\mathbf{P}$  is 3. Four very different initial guesses lead to the identical result when employing the structure-factor algorithm.

In Table 2 and Fig. 1 we give the results of using the  $1s$ ,  $2s$  and  $3s$  functions to fit the hydrogen-atom structure factors by varying  $\zeta$  from 0.9 to 7.0. Conventional least-squares analyses in which the only

imposed constraint is normalization were carried out for comparison. The agreement factors,

$$R = \frac{\sum_{\text{all reflections}} ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum_{\text{all reflections}} |F_{\text{obs}}|}, \quad (19)$$

are listed in addition to the lower half of the  $\mathbf{P}$  matrices and their eigenvalues. Sensible idempotent solutions are found for all systems in which a reasonable basis ( $0.9 \leq \zeta \leq 2.0$ ) is used, indicating the results are not overly sensitive to the basis set. We should emphasize that although in every case the greater flexibility of the not-idempotent density matrix allows it to fit the data more closely, never is this density matrix  $N$ -representable. Even an extraordinarily accurate fit to the density does not force the density matrix to become quantum mechanically acceptable. For  $\zeta = 5.00$  the

agreement index is very small,  $R = 0.0009$ , but the eigenvalues range from  $-0.8976$  to  $1.7974$ , whereas the only acceptable values are  $1.0$  and  $0.0$ . Although the density is quite good, the elements of the density matrix have no meaning as population coefficients. Throughout the set of not-idempotent matrices in Table 2 this problem manifests itself as negative diagonal elements which theoretically should be squares of real numbers and as elements larger than  $1.0$  which violate the necessity of having a normalized wave function.

The best idempotent fit was found at  $\zeta = 1.12$  with the contribution of the  $1s$  orbital predominating. This result is in accord with the notion that the hydrogen 'atom' in a  $\text{H}_2$  molecule should be similar to the free atom ( $\zeta = 1.00$ ) but somewhat more contracted. In contrast, the best non-idempotent fit is at  $\zeta = 5.00$ , which again indicates that physical interpretation of this result would be misleading.

Table 1. *Study of initial guess dependence for the hydrogen atom*

The matrix  $\mathbf{P}$  defines the density matrix, through  $\rho = \text{tr} \mathbf{P} \psi(\mathbf{r}) \psi^\dagger(\mathbf{r})$ . The row matrix of basis functions is  $\psi^\dagger = 1s, 2s, 3s, 4s$ .

$\mathbf{P}$	$P_{11}$	$P_{21}$	$P_{31}$	$P_{41}$	$P_{22}$	$P_{32}$	$P_{42}$	$P_{33}$	$P_{43}$	$P_{44}$
Initial guess 1	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Initial guess 2	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500
Initial guess 3	0.5000	0.5000	0.0000	0.0000	0.5000	0.0000	0.0000	0.0000	0.0000	0.0000
Initial guess 4	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.00
Solution	0.7688	-0.3670	-0.1791	-0.1048	0.1752	0.0855	0.0500	0.0417	0.0244	0.0143

Table 2. *Comparison of idempotent and not-idempotent matrices for the hydrogen atom*

The row matrix of basis functions is  $\psi^\dagger = 1s, 2s, 3s$ .

$\zeta$	$\mathbf{P}$ idempotent		Eigenvalues	$\mathbf{P}$ not idempotent		Eigenvalues
0.90	0.9483		1.0000	3.1923 (0.31)		57.940
	0.1983	0.0415	0.0000	-28.3055 (3.7)	-2.0229 (0.27)	-2.192
	0.0985	0.0206	0.0102	0.0000	48.6904 (6.2)	-0.7343 (0.15)
	$R = 0.118$				$R = 0.027$	
1.00	0.9460		1.0000	1.9893 (0.11)		26.8444
	0.2088	0.0460	0.0000	-12.9117 (1.3)	-0.9163 (0.10)	-0.9837
	0.0872	0.0192	0.0080	0.0000	22.3742 (2.2)	-0.3214 (0.06)
	$R = 0.049$				$R = 0.010$	
1.12	0.9936		1.0000	1.0448 (0.04)		2.1293
	-0.0395	0.0016	0.0000	-0.7032 (0.44)	-0.0445 (0.03)	-0.0403
	-0.0692	0.0028	0.0048	0.0000	1.3489 (0.74)	-0.0065 (0.02)
	$R = 0.006$				$R = 0.004$	
1.20	0.9977		1.0000	0.6566 (0.08)		8.9821
	-0.0333	0.0011	0.0000	-4.3608 (0.97)	0.3152 (0.07)	0.3457
	-0.0345	0.0012	0.0012	0.0000	-7.4685 (1.6)	0.1187 (0.04)
	$R = 0.015$				$R = 0.009$	
5.00	0.2267		1.0000	0.1340 (0.005)		1.7974
	-0.4055	0.7254	0.0000	-0.9715 (0.06)	0.6351 (0.004)	0.1002
	0.1042	-0.1864	0.0479	0.0000	0.8811 (0.09)	-0.2250 (0.002)
	$R = 0.028$				$R = 0.0009$	
7.00	0.0000		1.0000	-0.1522 (0.06)		6.4519
	-0.0055	0.8208	0.0000	3.0254 (0.78)	0.8543 (0.06)	0.5476
	0.0026	-0.3835	0.1791	0.0000	-5.4171 (1.3)	-0.2024 (0.03)
	$R = 0.085$				$R = 0.009$	

Although we have stressed the point that X-ray scattering data alone cannot be used to determine the density matrix without the appropriate quantum-mechanical restrictions, a lack of  $N$ -representability can also have dramatic effects upon the density. This is illustrated in Fig. 2 where the best least-squares fit leads to a density which is strongly negative at and near the nucleus. The basis set in this case is somewhat inappropriate for the problem  $\zeta = 7.00$ , but the agreement factor  $R = 0.009$  indicates a fairly good overall fit. Of course, a plot of the electron density of an idempotent matrix using such an inappropriate basis would also look bizarre (although not negative). The point of presenting Fig. 2, however, is to illustrate that a good fit to the experimental data as measured by  $R$  is not in itself sufficient to ensure a density that is adequate in all respects. We have found regions of negative density to be common for least-squares fits to this hydrogen-atom data even when better bases are used, although these regions will usually be in areas where the density becomes only slightly but significantly negative.

**B. Hydrogen molecule.** To test the convergence and properties of our algorithm for a two-center system, we constructed an arbitrary normalized idempotent density containing two electrons and two nuclear centers at

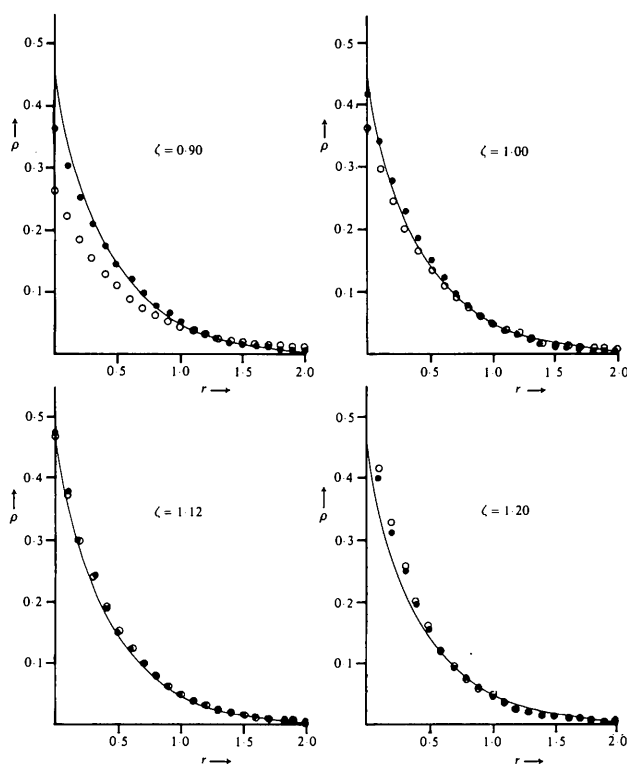


Fig. 1. Comparison of electron densities for the idempotent and not-idempotent matrices reported in Table 2 for the hydrogen atom. — Exact density; ● not-idempotent density; ○ idempotent density.

a distance of 1.23 atomic units. This density is defined by six basis functions which are Gaussian sums and have the symmetry of a ground-state  $H_2$  molecule. Since the operator matrices of (11) are complex for this system, intensity data were used. No initial guess dependence is found when the exact basis is used. The number of free parameters here is two. Four initial guesses converged to the exact solution although one initial guess failed to converge. Altering the basis so that the density could not be reproduced exactly (we multiplied all exponents by 1.05 in one case and 0.95 in another case) provided encouraging results. The exact density was reproduced very closely in all cases and only one initial guess did not lead to a solution identical to the others found in that basis. The bases

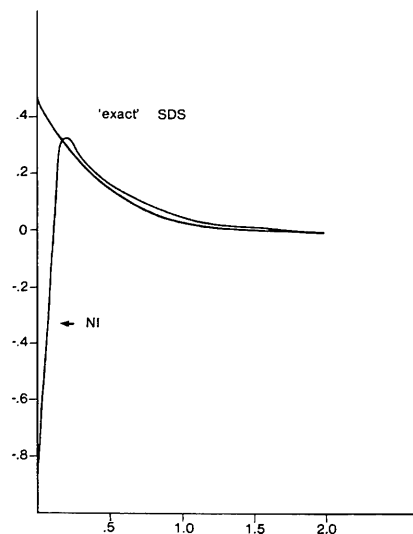


Fig. 2. Not-idempotent electron density for the scale factor  $\rho = 7.0$ .

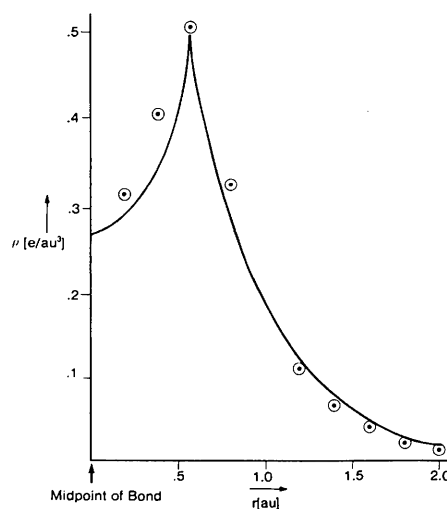


Fig. 3. Typical solution of  $P$  equations fit to  $H_2$  molecular density of Stewart, Davidson & Simpson (1965). The basis contains two  $1s$  functions with  $\zeta = 1.1$  and  $5.0$ , and one  $2s$  function with  $\zeta = 1.1$ . The agreement factor is  $R = 0.0225$ .

used in another case were the original functions with exponents multiplied by 0.85 and 1.5. They result in agreement factors of 0.0046 and 0.0048, respectively, again confirming that the application of this algorithm is not highly dependent upon having a good basis. These results indicate there is a possibility that the solution will depend upon the initial guess matrix, but there is not an infinity of solutions as would be expected in a typical unconstrained problem. To eliminate any possible arbitrariness, we suggest using a free variational calculation, either Hartree–Fock or some approximation to Hartree–Fock as an initial guess. This idea is an extension of the work of Henderson & Zimmerman (1976) which indicated the existence of continuous, noncrossing, idempotent, energy-property hypersurfaces. This means that if one starts with an idempotent matrix of lowest possible energy and changes its fit to X-ray scattering data in a slow quasi-continuous way, the result will be closest to the original matrix. To investigate a problem for which the exact solution is not idempotent, the spherical atomic scattering factors for hydrogen calculated by Stewart *et al.* (1965) were used to construct a set of molecular scattering factors at an interatomic distance of  $0.81 \times 1.4009$  atomic units. Scattering factors for nineteen values of  $\sin \theta/\lambda$  from 0.0215 to  $0.6011 \text{ \AA}^{-1}$  were used in four planes whose angles with the internuclear bond were 0, 20, 50 and  $90^\circ$ , to make a total of seventy-six scattering factors. Huzinaga's (1965) Gaussian expansions of STO's with variable exponential factors were used to expand the density matrix. In accord with previous results, good fits to the density were found to be not very sensitive to the details of the basis

functions. Limited experimentation with three atomic basis functions generally refined to  $R = 0.023$  regardless of exponents or type (1s, 2s, 3s). Presented in Fig. 3 is a typical result.

We thank Barbara Rubensohn for constructing Fig. 1, and Eric Unhjem and Toni Pezone for constructing Figs. 2 and 3, and CUNY-FRAP for grant support.

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*Acta Cryst.* (1982). **A38**, 98–102

## On the Estimation of $|E|$ Values of the Squared Structure on the Basis of Quartet Invariants

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(Received 9 July 1980; accepted 2 July 1981)

### Abstract

Expressions for the estimation of the  $|G_H|$  values, the  $|E_H|$  values of the squared structure, on the basis of all quartets in which  $H$  is a cross-term vector are presented

for the space groups  $P1$  and  $P\bar{1}$ . A reliable estimation procedure was developed employing the quartets with highest quartet product only. It appears that in this way  $|E|$  values of strong or weak reflections outside the limiting sphere could be predicted. An implication of