Determination of the Electron Density Matrix from X-Ray Diffraction Data

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We present a method for the conversion of x-ray diffraction data into an electron density which reflects the antisymmetry of the N-electron wave function.

In 1969 a series of papers[1] were published outlining a method for the direct determination of density matrices. In what follows we point out how the method may be used to convert coherent x-ray diffraction data into the electron density of the unit cell in any crystal and, therefore, in the constituent molecules.

The fundamental equation in x-ray structure work is

$$F(\vec{G}) = |F(\vec{G})| e^{i\varphi(\vec{G})} = \int d^3 r \, e^{i\vec{G}\cdot\vec{r}} \rho(\vec{r}), \qquad (1)$$

where $F(\vec{G})$ is, in general, the complex structure factor evaluated at the reciprocal lattice vector $\vec{G}$ and $\rho(\vec{r})$ is the electron density in the crystal.

Methods for direct determination of the density matrix via diffraction data[2] have commonly neglected the important quantum-mechanical condition of N representability. There is little hope that such inappropriate density matrices may be compared to those derived from wave functions. Recently, Jones and Lipscomb[3] have emphasized the importance in crystallography of using molecular densities that are properly N representable. They ensure this condition by working directly with antisymmetrized wave functions.

In the present note we suppose the structure to be known and use the diffraction data to directly fix the density matrix which has a form automatically ensuring N representability.

It is well known that the Hartree-Fock one-body density matrix satisfies $\rho(\vec{r}', \vec{r}) = \rho^*(\vec{r}, \vec{r}')$ and $\int d^3 r \, \rho(\vec{r}, \vec{r}) = N$ and is idempotent, i.e.,

$$\int d^3 r'' \rho(\vec{r}', \vec{r}'') \rho(\vec{r}'', \vec{r}) = \rho(\vec{r}', \vec{r}). \qquad (2)$$

This, of course, implies that a matrix representative $\underline{P}$ in any other basis must also have these properties since $\rho(\vec{r}', \vec{r}) = \text{tr}\underline{P}\psi^\dagger(\vec{r}')\psi(\vec{r})$. The converse is also true. That is, $\underline{P}^2 = \underline{P}$, $\underline{P} = \underline{P}^\dagger$, and $\text{tr}\underline{P} = N$ constitute conditions sufficient to ensure Hartree-Fock representability. This means that the coordinate-space representative $\rho(\vec{r}', \vec{r})$

is derivable from an N-electron single determinantal wave function $\Psi(1, ..., N)$ via $\rho(\vec{r}', \vec{r})$
$= N \int d(2 \cdots N) \Psi^*(\vec{r}', 2, ..., N) \Psi(\vec{r}, 2, ..., N)$.

We have shown[1] that the above conditions can be attained by reducing the quantity $\text{tr}(P^2 - P)^2$ to constraints of the form $\text{tr}\underline{P}\underline{A} = \langle A_{op} \rangle$ (including $\text{tr}\underline{P} = N$), where $A_{ij} \equiv (\psi_i, \bar{A}_{op}\psi_j)$. This leads to an iterative equation

$$\underline{P}_{n+1} = 3\underline{P}_n{}^2 - 2\underline{P}_n{}^3 + \sum_\alpha \lambda_\alpha{}^{(n)} \underline{A}_\alpha, \qquad (3)$$

where α labels the different constraints. This equation converges rapidly to idempotent solutions satisfying the appropriate constraints provided the Langrange multipliers $\lambda_\alpha{}^{(n)}$ are determined at every iteration by

$$\lambda_\alpha{}^{(n)} = \sum_\beta (\underline{\tau}^{-1})_{\alpha\beta} \Delta_\beta{}^{(n)},$$

where $\tau_{\alpha\beta} \equiv \text{tr}\underline{A}_\alpha\underline{A}_\beta$ and $\Delta_\beta{}^{(n)} \equiv \langle A_\beta \rangle - \text{tr}(3\underline{P}_n{}^2 - 2\underline{P}_n{}^3)A_\beta$, the latter tending to zero as $\underline{P}_n$ approaches solution. Now since $F(\vec{G}) = \int d^3 r \, e^{i\vec{G}\cdot\vec{r}} \rho(\vec{r})$, we can view $F(\vec{G})$ as one of the constraints and $e^{i\vec{G}\cdot\vec{r}}$ as one of the constraining operators in Eq. (3). Thus, if we define the matrix $f_{ij} \equiv (\psi_i, e^{i\vec{G}\cdot\vec{r}}\psi_j)$, then

$$F(\vec{G}) = \text{tr}\underline{P}\underline{f}(\vec{G}) = \sum_{ij} P_{ij} f(\vec{G}).$$

Inserting this expression into Eq. (3) we have

$$\underline{P}_{n+1} = 3\underline{P}_n{}^2 - 2\underline{P}_n{}^3 + \sum_{\vec{G}} \lambda^{(n)}(\vec{G})\underline{f}(\vec{G}). \qquad (4)$$

Since we expect the molecular electron density to be adequately represented in a Hartree-Fock approximation, then it is quite reasonable to expect that Eq. (4) will converge to an idempotent solution which also represents the experimental structure factors.

We wish to emphasize the importance of Eq. (4). Its solution gives an electron density which is consistent with the experimental structure factors and properly accounts for the antisymmetry requirement on the electronic wave function.

In order to illustrate the previous discussion

TABLE I. The elements of the density matrices as a function of the orbital exponent ξ.

ξ	$\underline{P}_{NI}$ (1s, 1s)	$\underline{P}_{NI}$ (1s, 2s)	$\underline{P}_{NI}$ (2s, 2s)	$\underline{P}_I$ (1s, 1s)	$\underline{P}_I$ (1s, 2s)	$\underline{P}_I$ (2s, 2s)
0.98	0.8654	0.4677	0.1345	0.9695	0.1719	0.0305
1.00	0.8989	0.3649	0.1010	0.9769	0.1502	0.0231
1.02	0.9301	0.2672	0.0698	0.9842	0.1246	0.0158
1.04	0.9589	0.1745	0.0410	0.9910	0.0943	0.0090

we present a numerical example based upon the work of Stewart, Davidson, and Simpson.[4] They have fitted by the method of least squares a density of the form $\rho(r_A) + \rho(r_B)$ to the essentially exact H_2 density of Kolos-Roothaan. In this way a "best" spherical-atom approximation to the bonded atom is obtained. The x-ray form factors for this "best" hydrogen-atom density will be used as constraints in the determination of a one-electron density matrix. The corresponding wave function will then represent the electronic state of a bound hydrogen atom as viewed by a beam of x rays.

We have selected an orthonormal two-function hydrogenic basis

$$\psi_{1s}(r) = (\xi^3/\pi)^{1/2} e^{-\xi r},$$

$$\psi_{2s}(r) = (\xi^3/8\pi)^{1/2} e^{-\xi r/2}(1 - \tfrac{1}{2}\xi r).$$

We represent the electron density in this basis as

$$\rho(\vec{r}', \vec{r}) = \mathrm{tr}\underline{P}\psi^\dagger(\vec{r}')\psi(\vec{r}),$$

where the form of the density matrix is

$$\underline{P} \equiv \begin{pmatrix} 1-p & q \\ q & p \end{pmatrix}. \tag{5}$$

The elements of the above matrix $\underline{P}$ are deter-

TABLE II. Comparison of selected exact and calculated scattering factors for $\xi = 1.0$. $\mathfrak{F}(F_{NI}) = 0.0029$; $\mathfrak{F}(F_I) = 0.0189$.

F_{NI}	F_I	F_{ex}	$(\sin\theta)/\lambda$ ($\mathrm{\AA}^{-1}$)
1.0000	1.0000	1.0000	0.
0.7726	0.7664	0.7752	0.1288
0.3296	0.3045	0.3301	0.3006
0.0714	0.0658	0.0744	0.5582
0.0206	0.0190	0.0208	0.8158
0.0076	0.0071	0.0066	1.0735
0.0034	0.0031	0.0027	1.3311
0.0017	0.0016	0.0015	1.5887

mined by a least-squares fit to the scattering factors of the "best" spherical hydrogen-atom density of Stewart, Davidson, and Simpson. This is done in two different ways. In the first the density matrix $\underline{P}_{NI}$ is nonidempotent, and is required to satisfy $\mathrm{tr}\underline{P}_{NI} = 1$ and $\underline{P}_{NI} = \underline{P}_{NI}^\dagger$. In the second the density matrix $\underline{P}_I$ is idempotent, in addition to satisfying the conditions $\mathrm{tr}\underline{P}_I = 1$ and $\underline{P}_I = \underline{P}_I^\dagger$. For this simple case of a 2×2 matrix we may ensure idempotency quite simply by the requirement $q = \pm p^{1/2}(1 - p)^{1/2}$. In general, of course, one cannot construct idempotent matrices so easily—thus, the need for Eq. (4).

Note that $\underline{P}_I$ contains only one parameter to be determined by the least-squares condition, while $\underline{P}_{NI}$ contains two such parameters. This is an example of the general fact that idempotency restricts the class of density matrices allowed and reduces the number of independent parameters contained therein. In addition, the problem of correlation of parameters when the least-squares matrix becomes nearly singular should be lessened. Indeed in the present example, there can be no correlation problem for $\underline{P}_I$ since there is only one parameter.

In both the nonidempotent and idempotent cases the best least-squares density matrix is defined by minimization of the functional

$$\mathfrak{F} = \sum_{\vec{G}} W(\vec{G})[F(\vec{G}) - \mathrm{tr}\underline{P}f(\vec{G})]^2,$$

where $F(\vec{G})$ is the scattering factor of Stewart, Davidson, and Simpson; $W(\vec{G}) = G^2$ is the weighting factor; and $f(\vec{G})$ is the matrix of Fourier trans-

TABLE III. Eigenvalues (N_1 and N_2) of $\underline{P}_{NI}$ and $\underline{P}_I$ for various values of orbital exponent ξ.

ξ	$\underline{P}_{NI}$		$\underline{P}_I$	
	N_1	N_2	N_1	N_2
0.98	1.0935	−0.0935	1.	0.
1.00	1.0407	−0.0407	1.	0.
1.02	1.0063	−0.0063	1.	0.
1.04	0.9909	0.0090	1.	0.

TABLE IV. Elements of the density matrix for systematic errors in the scattering factor data via $F \rightarrow SF$, $1.00 \leqslant S \leqslant 1.04$. The orbital exponent is in all cases $\xi = 1.0$.

S	$\underline{P}_{NI}(1s, 1s)$	$\underline{P}_{NI}(1s, 2s)$	$\underline{P}_{NI}(2s, 2s)$	$\underline{P}_I(1s, 1s)$	$\underline{P}_I(1s, 2s)$	$\underline{P}_I(2s, 2s)$
1.00	0.8989	0.3649	0.1010	0.9769	0.1502	0.0231
1.02	0.9172	0.3746	0.0827	0.9725	0.1634	0.0275
1.04	0.9359	0.3844	0.0640	0.9684	0.1748	0.0316

forms of products of our basis functions.

In Tables I–VI we present numerical results. In Table I we give $\underline{P}_{NI}$ and $\underline{P}_I$ for several values of the orbital exponent ξ. One notes that both $\underline{P}_{NI}$ and $\underline{P}_I$ are physically reasonable in the sense that the density represented corresponds essentially to a $1s$ state with a small amount of the $2s$ state mixed in to account for the molecular nature of the "best" spherical hydrogen density of Stewart, Davidson, and Simpson. In Table II the scattering factors F_{NI} and F_I for the densities of Table I ($\xi = 1.0$) are given and compared to the exact values of Stewart, Davidson, and Simpson. One notes that both $\underline{P}_{NI}$ and $\underline{P}_I$ give a good representation of the exact scattering factors although $\underline{P}_{NI}$ is on the average better as indicated by the value of the least-squares functional (see bottom of columns 1 and 2).

In Table III we list the eigenvalues of $\underline{P}_{NI}$ and $\underline{P}_I$. Here a striking effect of idempotency is apparent. *For all cases the eigenvalues of $\underline{P}_{NI}$ violate the rigorous quantum-mechanical condition that they must be either 0 or 1 in order that the density be derivable from a wave function.* Thus, methods[2] that follow the simple least-squares procedure used here in determining $\underline{P}_{NI}$ will always be in danger of quantum-mechanical invalidity. In the one-electron problem, idempotency ensures quantum-mechanical representability. In the many-electron problem, idempotency ensures only Hartree-Fock or single determinantal representability. In order to ensure N representability in general, one would have to work with inequalities on the eigenvalues of $\underline{P}$. Given the present accuracy of molecular-structure fac-

tors, the Hartree-Fock algorithm given in Eq. (4) is probably quite adequate.

In Table IV we illustrate changes in the density matrix induced by systematic errors introduced into the scattering factors of Stewart, Davidson, and Simpson via $F(\vec{G}) \rightarrow SF(\vec{G})$ for $1.00 \leqslant S \leqslant 1.05$. Such variations might be expected from errors in the experimental scale factor. The density matrix $\underline{P}_{NI}$ follows these errors more closely than does $\underline{P}_i$. Typically, for $\underline{P}_{NI}$ a 5% error in $F(\vec{G})$ induces approximately a 5% error in the principal element $\underline{P}_{NI}(1s, 1s)$. The corresponding element of $\underline{P}_I$ suffers only a 1% error. Thus, the very flexibility which allows $\underline{P}_{NI}$ to fit the exact $F(\vec{G})$ data better on the average also allows it to fit these systematic errors better.

In Table V we introduce a change in the scattering-factor data of the form $F(\vec{G}) \rightarrow \exp(-BG^2)F(\vec{G})$ for $0.0 \leqslant B \leqslant 0.4$. This would be analogous to a change caused by isotropic lattice vibrations such as those due to thermal effects. In the calculations of this table no temperature parameters are indroduced into the basis to compensate for the fictitious experimental temperature effect. Note that as B increases, both $\underline{P}_{NI}$ and $\underline{P}_I$ suffer significant changes away from their ideal values at $B = 0$. Table VI shows that at least in this simple case the temperature effect can be adequately compensated for by inclusion of an appropriate temperature factor in the basis. Here each basis function is modified by a temperature factor $\exp(-BG^2/2)$, where B is identical to that used to modify $F(\vec{G})$, i.e., $\psi_i \rightarrow \exp(-BG^2/2)\psi_i$. The variations in $\underline{P}$ are now insignificant, implying that the "experimental" temperature effect introduced in

TABLE V. Elements of the density matrix for changes in the scattering factor data via $F \rightarrow \exp(-BG^2)F$. The orbital exponent is $\xi = 1.0$.

B	$\underline{P}_{NI}(1s, 1s)$	$\underline{P}_{NI}(1s, 2s)$	$\underline{P}_{NI}(2s, 2s)$	$\underline{P}_I(1s, 1s)$	$\underline{P}_I(1s, 2s)$	$\underline{P}_I(2s, 2s)$
0.	0.8989	0.3649	0.1010	0.9769	0.1502	0.0231
0.2	0.9476	0.2400	0.0523	0.9846	0.1232	0.0154
0.4	1.0429	−0.0094	−0.0429	0.9976	0.0488	0.0024

TABLE VI. Elements of the density matrix for changes in the scattering factor data via $F \rightarrow \exp(-BG^2)F$, and for corresponding changes in the basis $\psi \rightarrow \exp(-B \times G^2/2)\psi_i$. The orbital exponent is $\xi = 1.0$.

B	$\underline{P}_{NI}(1s,1s)$	$\underline{P}_{NI}(1s,2s)$	$\underline{P}_{NI}(2s,2s)$	$\underline{P}_{I}(1s,1s)$	$\underline{P}_{I}(1s,2s)$	$\underline{P}_{I}(2s,2s)$
0.	0.8989	0.3649	0.1010	0.9769	0.1502	0.0231
0.2	0.8994	0.3641	0.1005	0.9771	0.1497	0.0229
0.4	0.8999	0.3631	0.1000	0.9772	0.1491	0.0228

Table V has been taken care of by the "theoretical" temperature factors in the basis. Of course, in an actual case the whole problem of how to account adequately for thermal effects will be quite complicated. The calculations of Tables V and VI are suggestive that a temperature-dependent basis of the form $\psi_i^T \equiv \psi_i \exp(-B_i G^2/2)$ will be useful in accounting for the temperature effect within the context of our formalism. This is analogous to the approach used by Coppens[2] who, however, assigned a temperature factor T_{ij} to each product $\psi_i^*\psi_j$. One might also allow each basis function to have a more complicated temperature dependence via their orbital exponents. There are yet other ways of including thermal factors. Since both the density matrix P and the basis ψ depend upon nuclear coordinates, the thermal average of the calculated density must be studied with some care. This is an especially important point since, as recently pointed out by Coppens,[2] aspects of molecular bonding can be spuriously represented by anisotropic thermal parameters.

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[1]W. L. Clinton, J. Nakhleh, and F. Wunderlich, Phys. Rev. 177, 1 (1969); see also L. J. Massa and W. L. Clinton, Trans. Amer. Crystallogr. Assn. 8, 149 (1972); W. L. Clinton and L. J. Massa, Int. J. Quantum Chem. 6, 519 (1972).

[2]P. Coppens, T. V. Willoughby, and L. N. Csonka, Acta Crystallogr. A27, 248 (1971); P. Coppens, L. Csonka, and T. V. Willoughby, Science 167, 1126 (1970); P. Coppens, D. Pautler, and J. F. Griffin, J. Amer. Chem. Soc. 93, 1051 (1971); P. Coppens, Science 158, 1577 (1967).

[3]D. S. Jones and W. N. Lipscomb, Acta Crystallogr. A26, 196 (1970.

[4]R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys. 42, 3175 (1965).

Anisotropic Ultrasonic Properties of a Smectic Liquid Crystal

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Ultrasonic measurements have been made in an oriented smectic liquid crystal. The material was aligned by cooling through the liquid crystal–isotropic liquid transformation in the presence of a 12.4-kOe magnetic field. The ultrasonic attenuation is significantly more anisotropic than it is in nematics. The velocity also has a measurable anisotropy ($\sim 5\%$). The velocities give certain of the elastic constants in de Gennes's theory of the smectic state.

There have been some ultrasonic measurements in smectic liquid crystals,[1-5] but in these studies no attempt was made to orient the molecules in the sample material. In this note, ultrasonic data are obtained for an oriented smectic; the material is oriented by cooling it through the

isotropic liquid–smectic transition in the presence of a large magnetic field. In this case the optic axis of the liquid crystal lies in the direction of the field, the same as for nematics.[6]

The experimental situation has already been described in an earlier publication.[7] A MATEC