

Idempotent density matrices for correlated systems from x-ray-diffraction structure factors

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X-ray structure-factor data can be used to obtain an electron-density matrix corresponding to a wave function that is a single determinant of orbitals. Equations are derived which treat this problem for the case of electronic open shells. The equations are solved for model numerical problems of lithium and beryllium atoms. For these cases the structure-factor data are obtained from essentially exact wave functions.

I. INTRODUCTION

We¹ have previously pointed out the need for a proper quantum-mechanical model for a charge density that is fit to accurate x-ray diffraction data. We have proposed that the first-order reduced density matrix be required to be idempotent. Although idempotency restricts the class of wave functions that give rise to such a density to a single determinant of molecular spin orbitals, such wave functions appear able to give an excellent fit to scattering factors of correlated systems. Gilbert² has conjectured that the electron density of any system can be exactly described by the electron density of a single determinant wave function and has presented a compelling plausibility argument to support this idea. The work of Henderson³ has shown that very accurate density-dependent properties can be obtained from single determinant wave functions. The advantage of an idempotent density matrix in x-ray analysis is that it allows one to correctly compare experimentally determined population coefficients to theoretical calculations, and in fact to calculate any property of the system. In this paper we generalize the formalism for obtaining an idempotent density matrix to treat open-shell systems that can be described by a single determinant. The form of the wave function is the same as that taken by Pople and Nesbet⁴ in the method known as unrestricted Hartree-Fock (UHF) or spin-polarized Hartree-Fock. In contrast to the UHF method where the parameters in the wave function are chosen so as to minimize the energy, we shall choose them so as to get the best fit, in an

average sense, to a set of x-ray diffraction data. In Sec. II we present the formalism for obtaining such a fit and in Sec. III we present the results as applied to the lithium and beryllium atoms.

II. FORMALISM

In the unrestricted Hartree-Fock method, the wave function is a single Slater determinant of N spin orbitals Φ_i , where N is the total number of electrons in the system. Each orbital consists of a space part times a spin function which may be either α or β spin, but there is no requirement that any space orbitals be doubly occupied. For such a wave function the first-order reduced density matrix will be a sum of the squares of the spin orbitals

$$\begin{aligned} \rho(1,1') &= \sum_{i=1}^N \Phi_i(1)\Phi_i^*(1') \\ &= \sum_{i=1}^{N_\alpha} \varphi_i(\vec{r}_1)\varphi_i^*(\vec{r}_1')\alpha(1)\alpha(1') \\ &\quad + \sum_{i=N_\alpha+1}^{N_\alpha+N_\beta} \varphi_i(\vec{r}_1)\varphi_i^*(\vec{r}_1')\beta(1)\beta(1'). \end{aligned} \quad (1)$$

N_α and N_β are the number of α and β electrons, respectively; $N_\alpha + N_\beta$ must of course equal N . It is natural to define the two spinless density matrices

$$\rho^\alpha(\vec{r}_1; \vec{r}_1') = \sum_{i=1}^{N_\alpha} \varphi_i(\vec{r}_1)\varphi_i^*(\vec{r}_1') \quad (2a)$$

and

$$\rho^\beta(\vec{r}_1; \vec{r}'_1) = \sum_{i=N_\alpha+1}^{N_\alpha+N_\beta} \varphi_i(\vec{r}_1) \varphi_i^*(\vec{r}'_1). \quad (2b)$$

Due to the orthonormality within the set of α -space orbitals and within the set of β -space orbitals, ρ^α and ρ^β must satisfy the following conditions of idempotency, normalization, and hermiticity:

$$\int \rho^\alpha(\vec{r}; \vec{r}') \rho^\alpha(\vec{r}'; \vec{r}'') d\vec{r}' = \rho^\alpha(\vec{r}; \vec{r}''); \quad (3a)$$

$$\int \rho^\beta(\vec{r}; \vec{r}') \rho^\beta(\vec{r}'; \vec{r}'') d\vec{r}' = \rho^\beta(\vec{r}; \vec{r}''),$$

$$\int \rho^\beta(\vec{r}; \vec{r}) d\vec{r} = N_\alpha;$$

$$\int \rho^\beta(\vec{r}; \vec{r}) d\vec{r} = N_\beta, \quad (3b)$$

$$\rho^\alpha(\vec{r}; \vec{r}') = \rho^\alpha(\vec{r}'; \vec{r}), \quad (3c)$$

In fact, should two density matrices satisfy all of conditions (3), they must be of the form of Eq. (2) and can be broken down into their constituent orbitals. Our task is to find a ρ^α and ρ^β subject to conditions (3) that give the best fit, in an average sense, to a set of crystallographically determined structure factors $F(\vec{S})$, the relationship being

$$F(\vec{S}) = \int [\rho^\alpha(\vec{r}; \vec{r}) + \rho^\beta(\vec{r}; \vec{r})] e^{i\vec{r} \cdot \vec{S}} d\vec{r}. \quad (4)$$

Toward that end we expand the space orbitals in an atomic basis set of size m $\{\psi\}$

$$\varphi_i(\vec{r}) = \sum_{\mu=1}^m c_{i\mu} \psi_\mu(\vec{r}), \quad i=1, N. \quad (5)$$

The set of equations (5) can be written more compactly in matrix form

$$\varphi = \underline{c} \underline{\psi}. \quad (6)$$

Here φ and $\underline{\psi}$ are column matrices of the space orbitals and basis functions, respectively, and c is the rectangular $N \times m$ matrix of expansion coefficients. The first N_α rows of \underline{c} comprise \underline{c}_α , while the remaining N_β rows comprise \underline{c}_β . The density ma-

trices are conveniently written as a trace

$$\rho^\alpha(\vec{r}; \vec{r}') = \text{tr} \underline{P}^\alpha \underline{\psi}(\vec{r}) \underline{\psi}^\dagger(\vec{r}'), \quad (7)$$

where \underline{P}^α is the $m \times m$ matrix representative of ρ^α in the $\underline{\psi}$ basis defined by

$$\underline{P}^\alpha \equiv (\underline{c}_\alpha)^\dagger \underline{c}_\alpha. \quad (8)$$

Similarly,

$$\rho^\beta(\vec{r}; \vec{r}') = \text{tr} \underline{P}^\beta \underline{\psi}(\vec{r}) \underline{\psi}^\dagger(\vec{r}'). \quad (9)$$

$$\underline{P}^\beta \equiv (\underline{c}_\beta)^\dagger \underline{c}_\beta. \quad (10)$$

Conditions (3) become the following matrix conditions:

$$(\underline{P}^\alpha)^2 = \underline{P}^\alpha; \quad (\underline{P}^\beta)^2 = \underline{P}^\beta \quad (11a)$$

$$\text{tr} \underline{P}^\alpha = N_\alpha; \quad \text{tr} \underline{P}^\beta = N_\beta \quad (11b)$$

$$(\underline{P}^\alpha)^\dagger = \underline{P}^\alpha; \quad (\underline{P}^\beta)^\dagger = \underline{P}^\beta \quad (11c)$$

for an orthonormal basis.

By defining the set of matrices $\underline{f}(\vec{S})$,

$$\underline{f}_{ij}(\vec{S}) \equiv \int \psi_i^*(\vec{r}) \psi_j(\vec{r}) e^{i\vec{r} \cdot \vec{S}} d\vec{r}, \quad (12)$$

Eq. (4) can also be written as a set of trace conditions

$$F(\vec{S}) = \text{tr}(\underline{P}^\alpha + \underline{P}^\beta) \underline{f}(\vec{S}). \quad (13)$$

Since the set of structure factors $F(\vec{S})$ contains experimental errors and the number of parameters is much less than the number of data points, we do not expect (13) to hold exactly for every reflection. Instead we seek to minimize the sum of deviations from (13)

$$\sum_{\vec{S}} |\text{tr}(\underline{P}^\alpha + \underline{P}^\beta) \underline{f}(\vec{S}) - F(\vec{S})| = \epsilon, \quad (14)$$

by choosing \underline{P}^α and \underline{P}^β subject to constraints (3) such that ϵ is a minimum. The absolute value is chosen for (14) to have a linear function of \underline{P}^α and \underline{P}^β and render the problem mathematically tractable.

The idempotency of \underline{P}^α and \underline{P}^β can be ensured by reducing the quantity $\text{tr}(\underline{P}^{\alpha^2} - \underline{P}^\alpha)^2 + \text{tr}(\underline{P}^{\beta^2} - \underline{P}^\beta)^2$ to zero and using the Lagrangian multiplier technique to enforce (11a) and (11b).

$$\delta \left[\text{tr}(\underline{P}^{\alpha^2} - \underline{P}^\alpha)^2 + \text{tr}(\underline{P}^{\beta^2} - \underline{P}^\beta)^2 - 2\lambda_1 \text{tr} \underline{P}^\alpha \underline{1} - 2\lambda_2 \text{tr} \underline{P}^\beta \underline{1} - 2\lambda_3 \left[\sum_{\vec{S}_+} \text{tr}(\underline{P}^\alpha + \underline{P}^\beta) \underline{f}(\vec{S}_+) - \sum_{\vec{S}_-} \text{tr}(\underline{P}^\alpha + \underline{P}^\beta) \underline{f}(\vec{S}_-) \right] \right] = 0 \quad (15)$$

where a reflection is in the \vec{S}_+ group if

$$\text{tr}(\underline{P}^\alpha + \underline{P}^\beta) f(\vec{S}) - F(\vec{S}) \geq 0 \quad (16)$$

and is in the \vec{S}_- group otherwise. To first order the variation yields

$$2 \left\{ \text{tr} \left[2\underline{P}^{\alpha^3} - 3\underline{P}^{\alpha^2} + \underline{P}^\alpha - \lambda_1 \underline{1} - \lambda_3 \left[\sum_{\vec{S}_+} f(\vec{S}_+) - \sum_{\vec{S}_-} f(\vec{S}_-) \right] \right] \delta \underline{P}^\alpha \right. \\ \left. + \text{tr} \left[2\underline{P}^{\beta^3} - 3\underline{P}^{\beta^2} + \underline{P}^\beta - \lambda_2 \underline{1} - \lambda_3 \left[\sum_{\vec{S}_+} f(\vec{S}_+) - \sum_{\vec{S}_-} f(\vec{S}_-) \right] \right] \delta \underline{P}^\beta \right\} = 0. \quad (17)$$

Since the variations $\delta \underline{P}^\alpha$ and $\delta \underline{P}^\beta$ are arbitrary and independent of each other, each expression in square brackets must be identically zero:

$$2\underline{P}^{\alpha^3} - 3\underline{P}^{\alpha^2} + \underline{P}^\alpha - \lambda_1 \underline{1} - \lambda_3 \underline{G} = 0, \quad (18a)$$

$$2\underline{P}^{\beta^3} - 3\underline{P}^{\beta^2} + \underline{P}^\beta - \lambda_2 \underline{1} - \lambda_3 \underline{G} = 0, \quad (18b)$$

where

$$\underline{G} \equiv \sum_{\vec{S}_+} f(\vec{S}_+) - \sum_{\vec{S}_-} f(\vec{S}_-). \quad (19)$$

Equations (18) can be solved iteratively according

to

$$\underline{P}_{n+1}^\alpha = 3\underline{P}_n^{\alpha^2} - 2\underline{P}_n^{\alpha^3} + \lambda_{1n} \underline{1} + \lambda_{3n} \underline{G}_n, \quad (20a)$$

$$\underline{P}_{n+1}^\beta = 3\underline{P}_n^{\beta^2} - 2\underline{P}_n^{\beta^3} + \lambda_{2n} \underline{1} + \lambda_{3n} \underline{G}_n. \quad (20b)$$

Note that the matrix \underline{G} changes upon each iteration since a reflection may go from the \vec{S}_+ to the \vec{S}_- group or vice versa. The Lagrangian multipliers are determined at each step by enforcing (11b) and (14) for \underline{P}^α and \underline{P}^β , which yield the following matrix equation:

$$\begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{pmatrix} = \begin{pmatrix} \text{tr} \underline{1} & 0 & \text{tr} \underline{G} \underline{1} \\ 0 & \text{tr} \underline{1} & \text{tr} \underline{G} \underline{1} \\ \text{tr} \underline{G} \underline{1} & \text{tr} \underline{G} \underline{1} & 2 \text{tr} \underline{G} \underline{G} \end{pmatrix}^{-1} \begin{pmatrix} N_\alpha - \text{tr}(3\underline{P}_n^{\alpha^2} - 2\underline{P}_n^{\alpha^3}) \underline{1} \\ N_\beta - \text{tr}(3\underline{P}_n^{\beta^2} - 2\underline{P}_n^{\beta^3}) \underline{1} \\ \epsilon + \sum_{\vec{S}_\pm} \pm F(\vec{S}_\pm) - \text{tr}(3\underline{P}_n^{\alpha^2} - 2\underline{P}_n^{\alpha^3} + 3\underline{P}_n^{\beta^2} - 2\underline{P}_n^{\beta^3}) \underline{G}_n \end{pmatrix}. \quad (21)$$

To summarize the procedure, one chooses an initial guess for \underline{P}^α and \underline{P}^β from which a value for ϵ [Eq. (14)] is determined. A smaller ϵ value is chosen and a new \underline{P}^α and \underline{P}^β determined via Eqs. (20) and (21). Equations (20) and (21) are applied repeatedly until $\text{tr}(\underline{P}^{\alpha^2} - \underline{P}^\alpha)^2$ and $\text{tr}(\underline{P}^{\beta^2} - \underline{P}^\beta)^2$ are as close to zero as desired (less than 1×10^{-11} is satisfactory for five-decimal-place accuracy in the elements of the \underline{P} matrix) and (14) is satisfied for the chosen ϵ . At this point ϵ is again decremented and (20) and (21) applied until convergence is obtained. By thus decreasing ϵ in a superiterative process, one arrives at idempotent \underline{P}^α and \underline{P}^β which yield the minimum ϵ . We point out that Eq. (20) must be solved simultaneously as they are coupled through the matrix \underline{G} (which requires \underline{P}^α and \underline{P}^β to decide whether a reflection is in the \vec{S}_+ or \vec{S}_- group) and λ_3 . If $N^\alpha = N^\beta$, Eqs. (20) reduce to the iterative equation for closed-shell systems.¹

The determinant of the matrix of traces in (21) is

$$\Delta = 2m [\text{tr} \underline{1} \text{tr} \underline{G} \underline{G} - \text{tr}(\underline{G} \underline{1})^2] \quad (22)$$

since $\text{tr} \underline{1} = m$. Scharz's inequality requires that (22) be greater than zero since the \underline{G} matrix cannot be proportional to the unit matrix in this case. Therefore, these iterative equations can and will converge quite independent of any correlation of parameters that might be present. The number of independent parameters to be determined is

$$p = mN - N^{\alpha^2} - N^{\beta^2}. \quad (23)$$

If the chosen basis is not orthogonal but has an overlap matrix defined by

$$\underline{S}_{ij} \equiv \int \psi_i^*(\vec{r}) \psi_j(\vec{r}) d\vec{r}, \quad (24)$$

then Eqs. (20) and (21) can still be used if \underline{P}^α , \underline{P}^β , and $f(\vec{S})$ are replaced by \underline{R}^α , \underline{R}^β , and $f'(\vec{S})$ according to

$$\underline{R}^\alpha = \underline{S}^{1/2} \underline{P}^\alpha \underline{S}^{1/2} \quad (25a)$$

$$\underline{R}^\beta = \underline{S}^{1/2} \underline{P}^\beta \underline{S}^{1/2} \quad (25b)$$

$$f'(\vec{S}) = \underline{S}^{-1/2} f(\vec{S}) \underline{S}^{-1/2}. \quad (25c)$$

At solution, \underline{P}^α and \underline{P}^β can be recovered by the reverse transformations.

For a multicenter basis, the structure factors may not be real and the $f(\vec{S})$ matrices will generally not be Hermitian. In this case the intensities should be used for data and the $\underline{f}(\vec{S})$ matrices replaced by the Hermitian operator matrices

$$\underline{\mathcal{L}}_n(\vec{S}) = \frac{1}{2} [f^+(\vec{S})\text{tr}(\underline{P}_n^\alpha + \underline{P}_n^\beta)\underline{f}_n(\vec{S}) + \underline{f}_n(\vec{S})\text{tr}(\underline{P}_n^\alpha + \underline{P}_n^\beta)f^+(\vec{S})], \quad (26)$$

which will change at each iterative step until $\underline{P}_{n+1}^\alpha = \underline{P}_n^\alpha$ and $\underline{P}_{n+1}^\beta = \underline{P}_n^\beta$. It is straightforward to include weighting factors so that more accurate pieces of data are given more importance in the fitting, or to emphasize different regions of space.

III. RESULTS AND DISCUSSION

The lithium and beryllium atoms served as test cases for the formalism presented in Sec. II. The scattering factors used as data were taken from Benesch and Smith⁵ who calculated correlated coherent scattering factors from natural orbital expansions of high-accuracy wave functions. The lithium wave function was Larsson's⁶ 100-term Hylleraas-type function which accounted for 99% of the correlation energy. For beryllium, Weiss's⁷ configuration-interaction wave function (93.06% of the correlation energy) was used. In both cases 108 scattering factors, from $\sin\theta/\lambda = 0.000 \text{ \AA}^{-1}$ to $\sin\theta/\lambda = 4.000$, were used and given weighting coefficients of unity. The basis sets used here are the near-Hartree-Fock bases of Clementi.⁸ In each case the initial guess used was the UHF solution and ϵ was slowly decreased from the UHF value

until an apparent minimum was reached. As can be seen from Table I, the value of the measure of fit parameter ϵ decreased by a factor of about 100 from the UHF value for both Li and Be. As discussed by Henderson,⁹ this should lead to the single-determinant wave function with the desired properties (in this case the best fit to the scattering data) whose energy is closest to the Hartree-Fock energy. Henderson's work is based on the conjecture of noncrossing-energy hypersurfaces in property space. In fact the x-ray-structure factor-fitted wave functions (XR) have energies only 0.0009–0.01% higher than the UHF determinant. There is, however, no guarantee that this procedure will produce the lowest possible ϵ or that the density matrices determined for the lowest ϵ found are unique.

The density-dependent properties studied, $\langle 1/r \rangle$ for Li and Be and $\langle r^2 \rangle$ for Li, show significant improvement over the UHF values. The expectation values for other density properties were not available for the exact wave functions and so comparisons could not be made. Since the density matrix was determined by getting the closest possible fit to the Fourier transform of the density at a number of discrete points, this improvement in density properties over the UHF wave function is not unexpected. Although average values of other powers of r could not be compared to the exact values, it is likely that they would also show improvement. Unequal weighting of the observed structure factors could be used to emphasize different regions of space. Structure factors for small values of $\sin\theta/\lambda$ contain significant contributions from the valence density, whereas structure factors for large values of $\sin\theta/\lambda$ do not. The weighting scheme used here emphasizes those structure fac-

TABLE I. Comparison of expectation values from the exact, Hartree-Fock, and x-ray-fitted densities for the lithium and beryllium atoms.

		ϵ	Total energy	Kinetic energy	$\langle \frac{1}{r_{12}} \rangle$	$\langle \frac{1}{r} \rangle$	$\langle r^2 \rangle$	Fermi contact term	$\langle S^2 \rangle$ (Atomic units)
Li	Exact	0.0000	-7.478 025	7.478	2.199	5.718 22	18.350 34	2.906	0.750 00
	HF	0.1506	-7.432 749	7.433	2.281	5.715 49	18.626 10	2.909	0.750 02
	XR	0.0020	-7.432 694	7.438	2.285	5.718 66	18.346 09	3.015	0.750 02
Be	Exact	0.0000	-14.660 90	14.66	4.3803	8.4246			
	HF	0.9945	-14.573 02	14.57	4.4891	8.4088	17.320 08		
	XR	0.0093	-14.571 50	14.59	4.5376	8.4255	16.320 10		

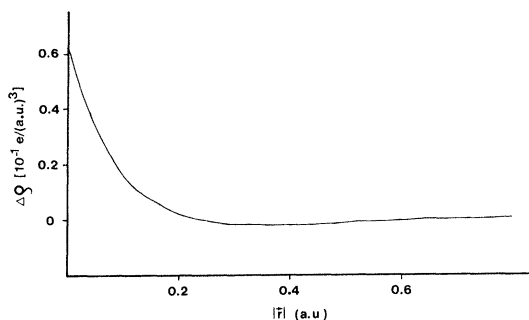


FIG. 1. $(\rho^{\text{XR}} - \rho^{\text{HF}}) \times 10$ for the ground-state lithium atom.

tors with the largest magnitude, hence the smaller values of $\sin\theta/\lambda$.

Figures 1 and 2 show the difference between the UHF and XR densities. The greatest absolute differences occur at the nucleus with a buildup of charge in the XR density. This buildup at the nucleus is balanced by a steep deficit between 0.08 and 0.4 a.u. in Be, and a shallow deficit between 0.23 and 0.60 a.u. in Li. At $r > 0.6$ a.u. the UHF and XR densities are virtually the same in Li. In Be this does not occur until 1.5 a.u.

For both atoms the UHF structure factors are most grossly in error in the region $0 < \sin\theta/\lambda < 0.7 \text{ \AA}^{-1}$ (Figs. 3 and 4). Benesch and Smith⁵ also report "best density" (BD) structure factors for Li. The BD wave function is obtained by taking the three natural spin orbitals with the highest occupation numbers in the exact first-order density matrix and forming their antisymmetrized product. According to a theorem by Löwdin¹⁰ this gives the best approximation (in an overlap sense) to $\rho_1(1;1')$. The BD structure factors for Li deviate significantly from the exact in the area around

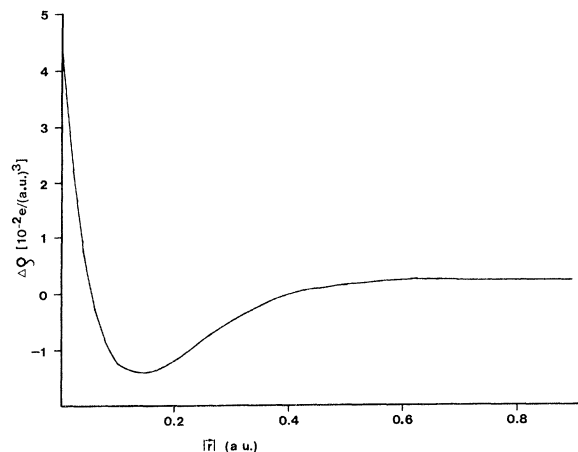


FIG. 2. $(\rho^{\text{XR}} - \rho^{\text{HF}}) \times 100$ for the ground-state beryllium atom.

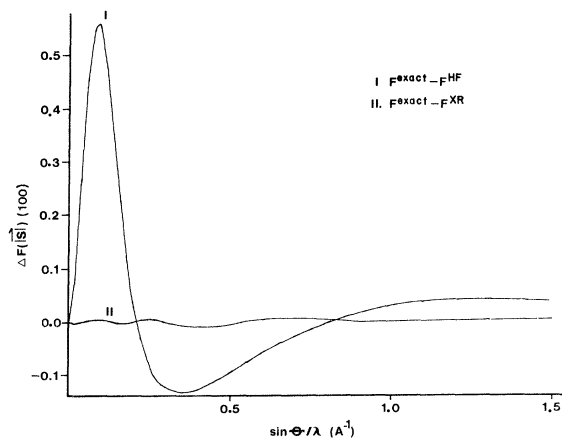


FIG. 3. Coherent x-ray scattering factor differences for ground state of the lithium atom.

$\sin\theta/\lambda = 0.5 \text{ \AA}^{-1}$ and fit worse than UHF in the area from $\sin\theta/\lambda = 0.45$ to 1.0 \AA^{-1} . The XR structure factors agree better than either the UHF or BD in all regions of reciprocal space and oscillate mildly around the exact values. The XR structure factors for Be fit better than the UHF and exhibit their maximum difference from the exact at about 0.07 \AA^{-1} . The kinetic energy, which depends upon the first-order density matrix (i.e., the off-diagonal elements) shows a slight improvement over the UHF values.

In contrast to the one-body properties, whose values appear to improve by structure factor fitting, two-body properties are worse than the UHF values. As previously mentioned the total energies of the two systems studied increased by less than 0.01% over UHF. Since kinetic and electron-nuclear attraction energies improved, this decrease

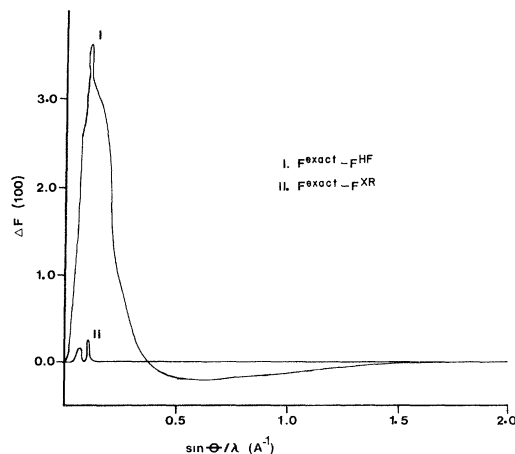


FIG. 4. Coherent x-ray scattering factor differences for the beryllium atom ground state.

in accuracy of the energy can be attributed to electron-electron repulsions. The average value $\langle 1/r_{12} \rangle$ increased for XR functions, indicating a less favorable r_{12} distribution. For Be, Benesch and Smith⁵ report total scattering intensities which are related to $\rho_2(1;2)$ by

$$\frac{I_{\text{tot}}}{I_{\text{cl}}} = N + 2 \int e^{i\vec{S} \cdot (\vec{r}_1 - \vec{r}_2)} \rho_2(1;2) d1 d2, \quad (27)$$

where I_{cl} is the classical scattering intensity of a free electron. For comparison we draw differences in I_{tot} between the exact wave function and the XR and UHF values in Fig. 5. The shapes of the difference curves are quite similar, yielding maximum errors at the same values of $\sin\theta/\lambda$.

Benesch and Smith attribute the peak at $\sin\theta/\lambda = 0.12 \text{ \AA}^{-1}$ to L -shell correlation, and the errors in the region $\sin\theta/\lambda = 3.0 \text{ \AA}^{-1}$ to K -shell correlation. At $\sin\theta/\lambda = 0.12 \text{ \AA}^{-1}$ the correlation distribution error is about three times that of the UHF value, although in the region $\sin\theta/\lambda = 0.37 \text{ \AA}^{-1}$ it is somewhat improved over UHF. For $\sin\theta/\lambda > 1.1 \text{ \AA}^{-1}$, UHF and XR give essentially identical values.

One of the major objections to the UHF method is that the wave function is not an eigenfunction of \hat{S}^2 . In this formalism the expectation value of \hat{S}^2 is given by

$$\langle \hat{S}^2 \rangle = \frac{1}{2}N + \frac{1}{4}(N^\alpha - N^\beta)^2 - \text{tr} \underline{P}^\alpha \underline{S} \underline{P}^\beta \underline{S}. \quad (28)$$

For the Be atom this is no problem if we start with an initial guess of $\underline{P}^\alpha = \underline{P}^\beta$. This is equivalent to enforcing double occupation of the orbitals, and the iteration will preserve this relation. For the Li atom, the UHF calculation gives a value for $\langle \hat{S}^2 \rangle$ of 0.7500158 that is very close to the value for a pure triplet, 0.750000. This value changes insignificantly to 0.7500152 in the XR function. The hyperfine splitting energy which arises from the Fermi contact term in the Li atom is a function of $(\rho^\alpha - \rho^\beta)$ evaluated at the nucleus. The magnitude of this quantity is generally much improved in the UHF function over the restricted Hartree-Fock value and is known to be very sensitive to the basis set used. In the one case tested here, Li, the XR value was significantly worse than the UHF value. It may be that an energy criterion such as is used

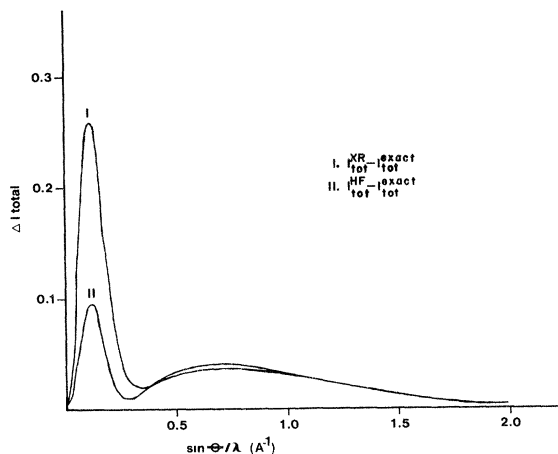


FIG. 5. Total scattering intensity differences for the beryllium atom ground state.

in determining the HF wave function, is a more stringent requirement on the density at the nucleus than x-ray scattering conditions. However, it appears from other expectation values that x-ray fitting will provide a better average density.

CONCLUSION

Very accurate one-body density-dependent properties can be obtained by fitting the parameters of an idempotent density matrix to an accurate set of x-ray-diffraction structure factors. Properties requiring the off-diagonal elements of the density matrix, e.g., kinetic energy, also appear to improve slightly over that obtained by a variational calculation of the energy. To pay for this improvement, the two-body distribution is not as good as that obtained by a variational calculation, although the total energy need not be dramatically increased. The need for a density matrix which takes into account electron correlation is apparently not necessary for an accurate description of the density.

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