Theor Chim Acta (1994) 88: 437–445

Theoretica Chimica Acta

Density matrices from position and momentum densities

W. H. E. Schwarz, A. Langenbach and L. Birlenbach
Theoretische Chemie, Universität, D-57068 Siegen, Germany

Received July 21, 1993/Accepted February 8, 1994

Summary. One-electron density matrices, which are representable in single-center s-orbital basis sets, have been investigated with respect to their reconstruction from densities. The maximum allowed dimension for reconstruction from a combination of position & momentum density dependent properties is only slightly bigger than the dimension in the case of position (or momentum) densities only. Since for a given one-particle basis of dimension M, the number of one-matrix elements which can be determined is also of order M only, while the total number of one-matrix elements is of order M^2, it is in general necessary to introduce severe constraints and restrictions. The accuracy demands on the data and algorithms increase exponentially for linearly increasing size of basis set.

Key words: Density matrix – Electron density – Momentum density

1 Introduction

The many-particle system is completely described by its many-particle density matrix. Concerning the kinetic and external-potential energies as well as all other one-particle properties, the reduced one-particle density matrix (one-matrix) is already sufficient. It also allows us to determine the inter-particle interaction energy at the Hartree–Fock level of approximation.

In recent years several efforts have been undertaken to reconstruct the one-matrix from experimental data, both by laying the theoretical foundations [1, 2] and by performing numerical calculations (e.g. [3, 4]). The achievements are not always free from possible criticism[1], and many open questions remain.

A major problem is the following: Let a finite one-particle Hilbert space of dimension M be given, spanned by a basis of position functions $\varphi_i(r), \{\varphi_i;\ i = 1,\ldots,M\}$. By a Fourier transformation we obtain the equivalent basis in momentum

---

[1] For instance, the kinetic bond energy obtained in Ref. [3b] is in error by one order of magnitude and is of wrong sign; the basis set used in Ref. [3f] is of single-zeta quality only; in the approach of Ref. [3e] a set of theoretical energy calculations is needed in addition. Furthermore it is rather common (see e.g. [3a,b,c,f,g]) to impose the idempotency constraint on the one-matrix, what is not advisable if one wants to achieve good accuracy [4].

space, $\{\psi_i(p)\}$. A basis to represent the one-matrix D consists of the product functions $\{\Phi_{ij}(r',r'') = \varphi_i(r')\cdot\varphi_j^*(r'')\}$ or $\{\Psi_{ij}(p',p'') = \psi_i(p')\cdot\psi_j^*(p'')\}$, respectively,

$$D \cong \sum_{ij} |\varphi_i(r') > d_{ij} < \varphi_j(r'')| \cong \sum_{ij} |\psi_i(p') > d_{ij} < \psi_j(p''). \qquad (1)$$

Harriman [1] has shown that the matrix elements d_{ij} can be determined from the (experimentally determined) position density

$$\varrho(r) = \sum_{ij} \varphi_i(r)\, d_{ij}\, \varphi_j^*(r) \qquad (2)$$

alone, provided the contracted product functions $\phi_{ij}(r) = \varphi_i(r)\varphi_j^*(r)$ are linearly independent. However, Schwarz and Müller [5] have shown that this is in general *not* the case for quantum chemically useful basis sets. The results of Morrison [3e] indicate that basis set optimization is not very efficient in this respect. Harriman [1] also pointed out that the products of harmonic oscillator functions or of spherical harmonics are severely linear dependent.

It has been proposed by Schmider et al. [4] that the one-matrix might be determinable from the combination of the position density $\varrho(r)$ and the momentum density

$$\pi(p) = \sum \psi_i(p)\, d_{ij}\, \psi_j^*(p)\,, \qquad (3)$$

or from some equivalent set of position & momentum properties. Numerical tests [4] have yielded two important results: (i) The restriction to idempotent (i.e. independent particle) density matrices, advocated for in any previous approaches (e.g. [3]), is not tolerable if one wants to obtain a reasonably accurate one-matrix which reproduces both position and momentum properties. (ii) It is only possible to determine the d_{ij} if one restricts oneself to a rather small subspace of $\{\Phi_{ij}\} \cong \{\Psi_{ij}\}$ which, however, is already sufficient to generate surprisingly accurate one-matrices.

We will here investigate numerically, which maximum possible dimension may be expected for a density matrix to be generated from densities.

2 Theory

Let us try to determine $D \cong (d_{ij})$ by a least squares procedure from a given set of position and momentum densities ϱ and π (cf. Eq. (2) of Ref. [4c]):

$$\Delta = |\varrho - \sum d_{ij}\varphi_i\varphi_j^*|^2 + |\pi - \sum d_{ij}\psi_i\psi_j^*|^2 = \text{Min}, \qquad (4)$$

with the following definition of the norm:

$$|f(x)|^2 = \int f(x)\cdot f(x)^* \cdot \omega(x)\,\mathrm{d}x. \qquad (5)$$

$\omega(x)$ is some weight function, for instance the experimental accuracy of ϱ and π. Setting the derivatives of Δ with respect to the d_{ij} equal to zero, and assuming for convenience that all quantities are real, one obtains the following set of linear equations:

$$\sum_{k\geq l} \{|\varphi_i\varphi_j\varphi_k\varphi_l| + |\psi_i\psi_j\psi_k\psi_l|\}(2-\delta_{kl})\cdot d_{kl} = \{|\varphi_i\varphi_j\varrho| + |\psi_i\psi_j\pi|\} \quad \text{for all } i \geq j \qquad (6)$$

or, in short hand notation,

$$A_{ij,kl} \cdot \boldsymbol{d}_{kl} = \boldsymbol{a}_{ij}\,, \tag{7}$$

the formal solution of which is

$$\boldsymbol{d}_{kl} = A^{-1}_{kl,ij} \cdot \boldsymbol{a}_{ij}\,. \tag{8}$$

The one-matrix elements d_{kl} are well defined, if the matrix A is not singular. If only one of the two densities π, ϱ is given, then this problem reduces to the question of singularity of the four-orbital overlap matrix, e.g. $|\varphi_i\varphi_j\varphi_k\varphi_l|$, i.e. of the linear independence of contracted product functions $\phi_{ij}(r)$. This had been investigated theoretically by Harriman [1] and numerically by Schwarz and Müller [5]. Here we extend this investigation to the combined π, ϱ problem Eqs. (6)–(8).

In practice the experimentally based $\tilde{a}_{ij}$ [Eqs. (6) and (7)] are contaminated with errors δa_{ij}, which results in errors δd_{kl} of the reconstructed density matrix:

$$\delta\boldsymbol{d}_{kl} = A^{-1}_{kl,ij} \cdot \delta\boldsymbol{a}_{ij}\,. \tag{9}$$

The coefficients of $\boldsymbol{a}, \tilde{\boldsymbol{a}}$ – and of $\boldsymbol{d}, \tilde{\boldsymbol{d}}$ if numerically stable – are typically of the order of 1 or smaller. The determination of $\tilde{\boldsymbol{d}}$ from $\tilde{\boldsymbol{a}}$ will numerically break down, if A^{-1} is nearly singular, i.e. has very large matrix elements. The largest ones are of the order of $1/\lambda_{\text{min}}$, where λ_{min} is the smallest eigenvalue of matrix A,

$$A\boldsymbol{x}_i = \boldsymbol{x}_i\lambda_i\,, \tag{10}$$

so that

$$A^{-1} = X\lambda^{-1}X^{+}\,. \tag{11}$$

In order to investigate the singularity of A^{-1}, the spectral norm

$$\lg \kappa_{\text{spectral}} = \lg(\lambda_{\text{Max}}/\lambda_{\text{min}}) \tag{12}$$

in useful [5], where λ_{Max} is the largest eigenvalue of A and lg means $\log_{10}$. If the product functions are orthonormal, $\lg\kappa$ is zero. The more linear dependent the set of product functions is, i.e. the more singular the matrix A^{-1}, the larger is $\lg\kappa$. The densities ϱ and π must be given to at least $\lg\kappa$ digits, and the numerical calculations must be performed with at least $\lg\kappa$ digits of accuracy, if d_{ij} should be determinable from Eqs. (4) or (8), i.e. if the density matrix should be determinable from the densities. For other choices of numerical stability indices than κ_{spectral}, see [8].

If the original basis $\varphi_i(r)$ is orthonormal, the product functions $\Phi_{ij}(r', r'')$, or equivalently $\Psi_{ij}(p', p'')$, are also orthonormal. They form the basis space $\mathscr{E}$ of dimension M^2 for the one-matrix (or of dimension $M(M+1)/2$ if we consider real hermitean, i.e. symmetric matrices). The contracted product functions $\phi_{ij}(r)$ or $\varepsilon_{ij}(p)$, however, are non-orthonormal. They (i.e. the position density, or the momentum density, resp.) determine the density matrix only in subspaces of $\mathscr{E}$: $\mathscr{P} \oplus \mathscr{L}$ or $\mathscr{Q} \oplus \mathscr{L}$, resp., see the Diagram (cf. Harriman [1b]). If both position & momentum densities are known simultaneously, the one-matrix is determined in subspace $\mathscr{P} \oplus \mathscr{Q} \oplus \mathscr{L} \oplus \mathscr{N}$. The spaces $\mathscr{P} \oplus \mathscr{L}$, $\mathscr{Q} \oplus \mathscr{L}$ and $\mathscr{P} \oplus \mathscr{Q} \oplus \mathscr{L} \oplus \mathscr{N}$ are spanned by those

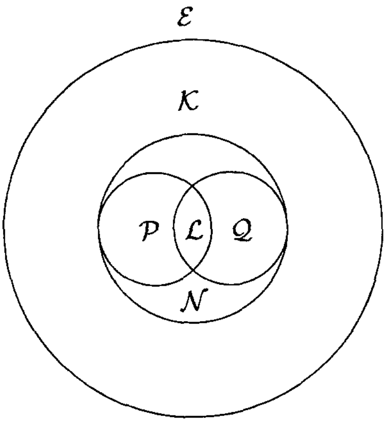

Diagram. Vector space $\mathscr{E}$ of one-matrices. Subspace $\mathscr{L}$ contains that part of the one-matrix which is equally determined by the position density as well as by the momentum density. $\mathscr{P} \oplus \mathscr{L}$(or $\mathscr{Q}$ $\oplus \mathscr{L}$) is determined by the position density (or, respectively, the momentum density). $\mathscr{P} \oplus \mathscr{Q} \oplus \mathscr{L} \oplus \mathscr{N}$ is determined by the combination of position & momentum densities. $\mathscr{K}$ contains that part of the one-matrix which remains undetermined. Compare Harriman [1b].

linear combinations of the Φ_{ij}, Ψ_{ij} and $\Phi_{ij} \oplus \Psi_{ij}$, which correspond to *orthonormal* linear combinations of the contracted functions $\phi_{ij}, \varepsilon_{ij}$ and $\phi_{ij} \oplus \varepsilon_{ij}$.

On the basis of numerical calculations with harmonic oscillator functions, Harriman [1b] found: For $\sim M$ one-particle basis orbitals φ and for $\sim M^2$ product basis functions Φ, only $\sim 2M$ one-matrix elements are determinable from a single density function and $\sim 4M$ one-matrix elements from a pair of densities, while $\sim (M-1)^2$ and $\sim (M-2)^2$ coefficients, respectively, for these two cases, remain undetermined. This means that, in the case of harmonic oscillator functions, a density matrix of dimension $\sim \sqrt{2M} \times \sqrt{2M}$ can be obtained from a density represented by M basis functions, and a density matrix of dimension $2\sqrt{M} \times 2\sqrt{M}$ from the combination of position and momentum densities.

If only a finite accuracy δ of the input data and a finite accuracy κ of the algorithm is given, only subspaces of $\{\Phi_{ij}\}, \{\Psi_{ij}\}$ or $\{\Phi_{ij} \oplus \Psi_{ij}\}$ of dimension $d_{\text{num}}(\Phi), d_{\text{num}}(\Psi)$ or $d_{\text{num}}(\Phi \oplus \Psi)$ can be handled numerically, namely the ones spanned by linear combinations x_i with eigenvalues $\lambda_i > \delta$ or κ. All other linear combinations (i.e. corresponding linear combinations of one-matrix elements d_{ij}) are completely undetermined.

3 Calculations

For our test calculations we use an even tempered set of one-center s-type Gaussian basis functions

$$\varphi_i(r) = C_i \exp(-\zeta_i r^2) \quad i = 1, \cdots, M, \tag{13a}$$

$$\zeta_i = \tfrac{1}{2}\alpha \cdot b^i \quad \text{with} \quad \alpha = b ** \left(-\tfrac{M+1}{2}\right), \tag{13b}$$

C_i is the normalization constant. For this special choice of ζ_i and α, the Fourier-transformed basis in momentum space is simply given by

$$\psi_i(p) = \varphi_{M+1-i}(p) \tag{14}$$

so that position and momentum spaces are represented by the same functions. Furthermore, we choose a constant weight function $\omega = 1$ for the definition of the norm [Eq. (5)]. Finally, one may renormalize the contracted product functions $\phi_{ij}(r) = \varphi_i(r)\varphi_j(r)$ and $\varepsilon_{ij}(p) = \psi_i(p)\psi_j(p)$ so that $\langle \phi_{ij} | \phi_{ij} \rangle = \langle \varepsilon_{ij} | \varepsilon_{ij} \rangle = 1$. The A-matrices for $\{\varphi\}, \{\psi\}$ and $\{\varphi \oplus \psi\}$ were calculated and then diagonalized.

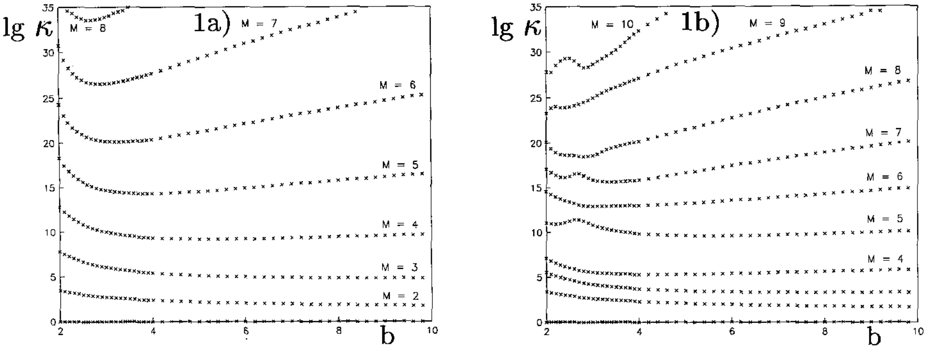

Fig. 1. $\lg\kappa$ as a function of the basis set parameter b [Eq. (12)] for different sizes of basis sets $M = 1$ to 10: (a) position space (or momentum space); (b) combined position & momentum space. See Eqs (12) and (13)

The computations were performed on a VAX computer with quadruple accuracy (about 33 decimal digits).

The basis set (13) is rather special with respect to three points. First, the eigenvalue spectra of our $\{\varphi(r)\}$ and $\{\psi(p)\}$ are the same. We note, that the functional similarity of position and momentum functions as in Eq. (14) also occurs for the spherical harmonics, which are the appropriate factors in general atomic orbital basis sets, or for the harmonic oscillator functions. Second, the basis is of one-center and s-type, as several ones investigated by Harriman [1]. Such basis sets are useful for small atoms, and our conclusions are relevant for atoms and the inner core shells of molecules, while molecular valence shells deserve further investigations. Preliminary analysis of more general basis sets [5] have shown that the problems of uniqueness and stability become even more serious. Third, the basis set is of the even tempered kind, which does not seem to pose a serious limitation.

4 Results

Numerical results are shown in Fig. 1. The $\lg\kappa$ versus b curves for different basis sizes M on the right chart (combined densities fitting) are lower than those on the left chart (single density fitting). This means: The determination of the density matrix D from position & momentum densities is numerically better conditioned than the determination of the density matrix from the position (or momentum) density alone.

To give an impression, we present spectral norms of A-matrices in Fig. 2, where statistical errors of the order of $\delta = 10^{-7}$ have been added to the matrix elements. The eigenvalues of an unmodified A-matrix are ≥ 0. The eigenvalues of the modified matrix are modified also by the order of δ, i.e. the smaller eigenvalues of A are now in the range of about $+\delta$ to 0 to $-\delta$. That is, the calculated inverse $\tilde{A}^{-1}$ becomes physically meaningless, and simultaneously $\lg\kappa$ becomes imaginary. For errors of $\sim 10^{-7}$ this happens already for more than 3 basis functions when fitting the density matrix to a single density, and for more than 4 to 5 basis functions when fitting to a pair of densities.

This difference in allowed dimensions becomes significant only for larger sizes of basis sets, which require numerical accuracies that are hardly accessible for

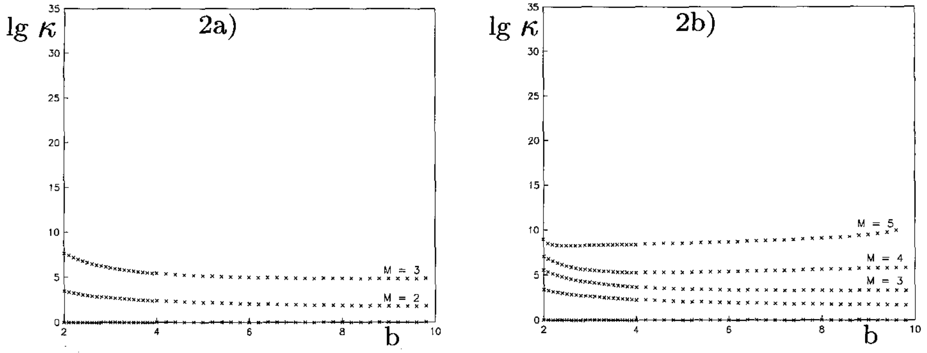

Fig. 2. Same as Fig. 1, but the A-matrix elements are modified statistically by errors $\varepsilon[\pm 10^{-7}]$. For larger M, $\lg\kappa$ is no longer real

experimental densities. $\lg\kappa$, i.e. the necessary accuracy in order to determine the one-matrix from the position or the momentum density alone, and from the combined densities, is shown in Fig. 3 as a function of the size of the basis set. These curves were generated for basis set parameter b=3, which yields reasonably flexible quantum chemical basis sets. [We note the somewhat oscillatory behavior of the results for the combined density fitting, for the special type of basis sets defined by Eq. (13), see also Fig. 1b.]

So, in general one must be content with determining D in a subspace only (of dimension d_{num}) of the full space $\mathscr{E}$ of dimension $M(M+1)/2$. Within this subspace, D is given by

$$d_{kl} = \sum_{ij} \sum_{m}^{\lambda_m/\lambda_{\text{Max}} > \delta} X_{kl,m} \cdot \lambda_m^{-1} \cdot X_{ij,m} \cdot a_{ij}, \tag{15}$$

where δ is the managable accuracy, while all contributions to D of the kind

$$\Delta d_{kl} = \sum_{m}^{\lambda_m/\lambda_{\text{Max}} < \delta} X_{kl,m} \cdot z_m, \tag{16}$$

with indeterminate numbers z_m, are completely unknown. The λ's are rather evenly distributed on a logarithmic scale, with only little clustering and with only slow

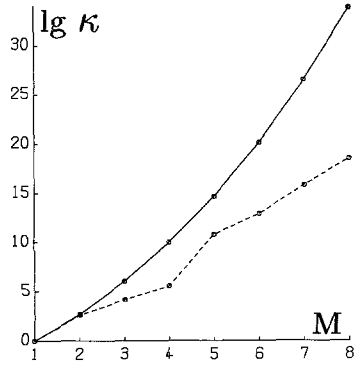

Fig. 3. $\lg\kappa$ as a function of basis set size M: (——) single density case, (······) combined position & momentum density case. $b = 3$

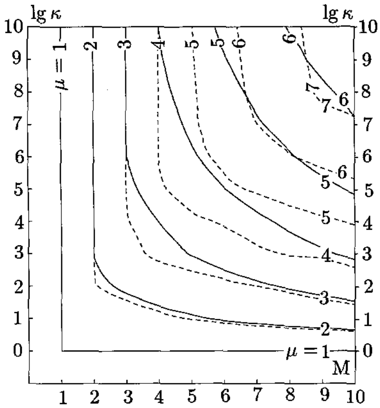

Fig. 4. Contour lines $\mu = 1,2,3,\ldots$ for the dimension $d_{\text{num}} = \mu(\mu+1)/2$ of density matrices which can be reconstructed from the position or the momentum density (——), and from the combined position & momentum density (– – – – – –) within a product function space $\mathscr{E}$ from M one-particle basis functions, if the accuracy is $\lg\kappa$ digits, see text

increase of λ_{m-1}/λ_m for increasing $1/\lambda_m$. So there are in general not just a single or a few eigenvalues which are smaller than the accuracy threshold.

From M basis functions, one obtains $M(M+1)/2$ product functions. We choose $d_{\text{num}} \le M(M+1)/2$ linear combinations of them to be used in Eq. (15). They correspond to the d_{num} eigenvectors $\boldsymbol{x}_i$ with largest eigenvalues λ_i. The required accuracy is $\delta \le \lambda_i/\lambda_{\text{Max}}$. We represent d_{num} by $\mu(\mu+1)/2$ with $\mu \le M$. In Fig. 4 we plot the accuracy parameter $\lg\kappa = \lg(1/\delta)$ for different one-particle basis size M and given $d_{\text{num}} = \mu(\mu+1)/2$. If we use only one kind of density, d_{num} represents the dimensions of space $\mathscr{P}\oplus\mathscr{L}, d_{\text{num}}(\Phi_{ij})$, which is equal to the dimension of space $\mathscr{Q}\oplus\mathscr{L}$ for our special choice (13) of one-particle basis, $d_{\text{num}}(\Psi_{ij})$. This d_{num} is represented by the full curves. If we exploit both kinds of densities, d_{num} is the dimension of space $\mathscr{P}\oplus\mathscr{Q}\oplus\mathscr{L}\oplus\mathscr{N}$, $d_{\text{num}}(\Phi_{ij}\oplus\Psi_{ij})$. This d_{num} is represented by the broken curves, which lie below the full ones.

A rough approximation of d_{num} is

$$d_{\text{num}}(\Phi \text{ or } \Psi) \approx 1 + \tfrac{4}{15}\lg\kappa \cdot M, \tag{17a}$$

$$d_{\text{num}}(\Phi\&\Psi) \approx 1 + \tfrac{5}{15}\lg\kappa \cdot (M+1). \tag{17b}$$

While the number of independent density matrix elements is of order M^2, namely $M(M+1)/2$, only a much smaller number of order M can be determined from a set of position or/and momentum density observables. The number of density matrix elements which can be determined from the combination of position and momentum densities is only slightly larger than from one density alone.

5 Summary

The most important result of this investigation on one-center s-type basis sets is that – although the combination of position and momentum densities improves the numerical determinability of density matrices – the general problem is not solved, namely that the necessary accuracy of the data increases exponentially in both cases with the size of basis set to be used. Without introducing some special constraints, only so few basis functions per atomic center are allowed that not more than one or at most two electronic shells per atom can be handled. We do not expect that this statement has to be changed if more general basis sets are investigated, which are needed for real molecules.

Different constraints have been proposed in the literature in order to fix those linear combinations of d_{ij} which are undetermined by the experimental data. The idempotency constraint on the density matrix [3a,b,c,f,g] is physically unfounded and has been proven unsuitable by numerical calculations [4].

Koga et al. [6a] apply a correction factor to a model wave function so that a given single density is recovered. (He then calculates other expectation values from this experimentally corrected model wavefunction.) This idea can be extended to apply a correction factor to a model one-matrix so that both the given momentum and position densities (and possibly other selected one-particle expectation values) are exactly recovered. Thereby, previous experience with model one-matrices could be accounted for. Gadre et al. [6b] have shown how to construct an approximate one-matrix from the position density by exploiting density functional experience with exchange-correlation functionals.

Collins [7] has introduced the idea of keeping the entropy of the density maximal. Finally one should account for the N-representability of the one-matrix, i.e. positive definiteness and possibly further restraints on the eigenvalues of the one-matrix, as discussed, e.g. in [9] in order to guarantee, for instance, that probabilities are positive. In view of Eq. (16) this restraint is, however, not very serious, if many degrees of freedom, namely $M(M+1)/2 - \mu/(\mu+1)/2$ ones, exist for the one-density matrix elements.

Schmider et al. [4] have successfully introduced the following constraints: a) fix the inner core density contribution to theoretical Hartree–Fock values; b) choose a one-particle basis for the valence shell which is known from previous SCF and CI-experience to be just flexible enough to yield reasonable accuracy in quantum chemical calculations; c) represent the valence shell contribution to the density matrix within a small MCSCF-type space, i.e. search for a small one-particle subspace within the given one-particle basis-space to construct $\mathscr{E}$-space which is known – from previous CI-experience – to be just big enough to describe the most prominent many-particle effects reasonably. The number of one-matrix parameters which could be determined seems to be of order M.

Given a one-particle basis of size $M, \varrho(r)$ is represented by a number of coefficients of order $O(M)$, and $\pi(p)$ is also represented by $O(M)$ coefficients. However it is impossible to determine the $O(M^2)$ unknown density matrix elements uniquely from the $O(M)$ given density coefficients, if M is larger than, say, $M = 3$. Approximate density matrices for atoms in molecules and crystals have been determined routinely from experimental and theoretical position densities [9–12]. Only a single basis function for any atomic ml-valence shell has been used there, namely the highest occupied atomic Hartree-Fock ground state eigenfunctions. The effective $M(M = 1$ or $M = 1$ *to* $2)$ is there so small, that no numerical problems arise.

For a given accuracy, only $O(\mu^2)$ matrix elements can be determined, where μ was defined above. For a harmonic oscillator basis [1b] $\mu(\Phi$ or $\Psi) \approx \sqrt{2M}$ and $\mu(\Phi \& \Psi) \approx 2\sqrt{M}$. Here the combination of both densities gives an improvement of $\sqrt{2} \times \sqrt{2}$. However, it is well known, that the higher eigenfunctions of a model Hamiltonian (of the harmonic oscillator or of the hydrogenic ion, for instance) form a very slowly convergent basis for the "perturbed" groundstate of the model Hamiltonian, i.e. it is already known beforehand that many matrix elements are very small. Better convergent basis sets as for instance the even tempered ones used in the present investigation yield $\mathscr{P} \oplus \mathscr{Q} \oplus \mathscr{L} \oplus \mathscr{N}$-spaces which are not

$\sqrt{2} \times \sqrt{2} = 1.4 \times 1.4$ times as big as the $\mathscr{P} + \mathscr{L}$-spaces, but only $f \times f$ times as big, where $f = \sqrt{d_{\text{num}}(\Phi \& \Psi)/d_{\text{num}}(\Phi)} \approx 1.2$ for reasonable values of M and κ, according to Eqs. (17). In these cases, the combination of two densities improves the determination of the one-matrix only slightly.

Acknowledgement. We are grateful to Professor Harriman, to a referee and to Dozent Jaquet for comments and to the Fonds der Chemischen Industrie for financial support.

References

1. (a) Harriman JE (1986) Phys Rev A 34:29; (b) Harriman JE (1993) Z Naturforsch A 48:203
2. (a) Erdahl R, Smith VH, Jr (Eds) (1987) Density matrices and density functionals. Reidel, Dordrecht; (b) Levy M, Goldstein JA (1987) Phys Rev B 35:7887
3. (a) Clinton WL, Massa LJ (1972) Phys Rev Lett 29:1363; (b) Massa L, Goldberg M, Frishberg C, Boehme RF, La Placa SJ (1985) Phys Rev Lett 55:622; (c) Frishberg C (1986) Int J Quantum Chem 30:1; (d) Tanaka K (1988) Acta Cryst A 44:1002; (e) Morrison RC (1988) Int J Quantum Chem Symp 22:43; (f) Aleksandrov YV, Tsirel'son VG, Reznik IM, Ozerov RP (1989) Phys Stat Sol b 155:201; (g) Pecora LM (1986) Phys Rev B 33:5987
4. (a) Schmider H, Smith VH, Weyrich W (1990) Trans Amer Cryst 26:125; (b) Schmider H, Smith VH, Weyrich W (1992) J Chem Phys 96:8986; (c) Schmider H, Smith VH, Weyrich W (1993) Z Naturforsch A 48:211; (d) Schmider H, Smith VH, Weyrich W (1993) Z Naturforsch A 48:221
5. Schwarz WHE, Müller B (1990) Chem Phys Lett 166:621
6. (a) Koga T, Yamamoto Y, Kryachko ES (1989) J Chem Phys 92:4758; (b) Gadre SR, Chakravorty SJ (1987) J Chem Phys 86:2224
7. Collins DM (1993) Z Naturforsch A 48:68
8. Engeln-Müllges G, Reutter F (1993) Numerik-Algorithmen, 7th ed. BI-Wissenschafts verlag, Mannheim
9. Schwarz WHE, Ruedenberg K, Mensching L (1989) J Am Chem Soc 111:6926
10. (a) Irle S, Lin HL, Niu JE, Schwarz WHE (1992) Ber Bunsenges Phys Chem 96:1545; (b) Schwarz WHE (1988) Portgal Phys 19:429; (c) Schwarz WHE, Ruedenberg K, Mensching L, Miller LL, Jacobson R, Valtanzanos P, von Niessen W (1989) Angew Chem Int Ed Engl 28:597
11. (a) Niu JE (1994) Doctoral Dissertation, University Siegen; (b) Niu JE, Schwarz WHE (1993) J East China Normal Univ (Nat Sci) 2:48
12. Schwarz WHE, Lin HL, Irle S, Niu JE (1992) J Mol Struct (Theochem) 255:435

Note added in proof. We do not support the recent statements of A. Soirat, M. Flocco and L. Massa, Int. J. Quantum Chem. (1994) 49:291 that 1) the finite number of experimentally obtainable x-ray scattering factors $F(k_i), i = 1, \ldots, n$, is sufficient to determine the exact density $\varrho(r)$, that 2) the density $\varrho(r)$ determines a Slater determinant uniquely, and that 3) the F's are even sufficient to obtain the correct (i.e. correlated density kernel $\varrho(r', r'')$.