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Direct Determination of Pure-State Density Matrices. II. Construction of Constrained Idempotent One-Body Densities[*]

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A formalism is developed for the determination of a constrained idempotent one-body density matrix $\underline{P}$. The method ensures pure-state representability in the Hartree-Fock sense. This is accomplished by minimizing the quantity $\mathrm{Tr}(\underline{P}^2-\underline{P})^2$ subject to either empirical or theoretical constraints. The method leads to an iterative matrix equation of the form

$$\underline{P}_{n+1}=3\underline{P}_n{}^2-2\underline{P}_n{}^3+\sum_k\lambda_k{}^{(n)}\underline{O}_k,$$

where $-\lambda_k$ is the kth Lagrangian multiplier pertaining to the constraint $\mathrm{Tr}\underline{P}\underline{O}_k=O_k$, and O_k is the expectation value of the observable $\underline{O}_k$. Applications to several diatomic molecules are reported using the electrostatic and virial theorems as empirical constraints. Several calculations are carried out in order to corroborate the following result: If the above iterative equations are constrained with a sufficient number of *bona fide* Hartree-Fock conditions, the solution is the Hartree-Fock $\underline{P}$ matrix.

I. INTRODUCTION

In paper I[1] of this series, semiempirical electron densities were given for some small molecules. It was pointed out that the method did not ensure N representability, i.e., there was no restriction that the natural spin-orbital occupation numbers n_k be bounded as $0\leq n_k\leq 1$, a necessary fermion condition. Indeed, some of the calculated n_k were negative. We could have avoided this difficulty by the expedient of working in terms of the parameters of a given wave function. However, in the authors' opinion, a direct determination of the density matrix has both computational and theoretical advantages.

The present paper is devoted to developing and applying a semiempirical method that avoids the previous occupation number difficulty. Thus a technique is introduced that ensures not only that $0\leq n_k\leq 1$ but also that a subset of the occupation numbers n_{k_occ} be unity, whereas the complementary subset n_{k_unocc} are zero. This is accomplished by imposing an idempotency condition on the density matrix. That is, we ensure single configuration or Hartree-Fock N representability.

In the single-configuration approximation, the one-body density matrix in the continuous representation is given by

$$\rho_1(1',1)=\sum_{k=1}^{N}\phi_k{}^*(1')\phi_k(1),\tag{1}$$

where $\langle k'|k\rangle=\delta_{kk'}$. Equation (1) implies that $\rho_1(1',1)$ is Hermitian, idempotent, and normalized to N. That the converse is also true has been shown by McWeeny.[2] Thus if we develop a method that ensures idempotency of $\rho_1=\rho_1{}^\dagger$ subject to $\mathrm{Tr}\rho_1=N$, then pure configuration representability is also ensured.

II. CONSTRAINED VARIATIONAL PRINCIPLE FOR THE DENSITY MATRIX

We define $\underline{P}$, the representative of ρ_1 in the discrete basis $\underline{\psi}$, such that $\rho_1(1',1)=\mathrm{Tr}\underline{P}\underline{\psi}^\dagger(1')\underline{\psi}(1)$. Following McWeeny we propose to ensure idempotency of P by reducing the scalar quantity $\mathrm{Tr}(\underline{P}^2-\underline{P})^2$ to zero. Consider the following stationary condition

$$\delta\mathrm{Tr}(\underline{P}^2-\underline{P})^2=2\mathrm{Tr}(\underline{P}^2-\underline{P})\delta(\underline{P}^2-\underline{P})=0.\tag{2}$$

But $\delta(\underline{P}^2-\underline{P})$ is an arbitrary variation, and, Eq. (2), therefore, is satisfied only if $(\underline{P}^2-\underline{P})\equiv 0$.[3] Thus stationarity of $\mathrm{Tr}(\underline{P}^2-\underline{P})^2$ with respect to variations in $(\underline{P}^2-\underline{P})$ ensures idempotency. In order to generate a more useful result, we must now consider variations with respect to $\underline{P}$. We therefore require

$$\delta\mathrm{Tr}(\underline{P}^2-\underline{P})^2=2\,\mathrm{Tr}(2\underline{P}^3-3\underline{P}^2+\underline{P})\delta\underline{P}=0.\tag{3}$$

The arbitrariness of $\delta\underline{P}$ implies as usual that the matrix in square brackets must be null. That is,

$$2\underline{P}^3-3\underline{P}^2+\underline{P}=(2\underline{P}-\underline{1})(\underline{P}-\underline{1})\underline{P}=\underline{0}.\tag{4}$$

The three solutions $\underline{P}=\tfrac{1}{2}\underline{1},\ \underline{1},\ \underline{0}$ of Eq. (4) are trivial. Note also that one of the trivial solutions, $\tfrac{1}{2}\underline{1}$, is not idempotent. Thus, in general, the solutions of Eq. (3) contain those of Eq. (2), but the converse is not true. All of the solutions of Eq. (4) can be obtained iteratively as

$$\underline{P}_{n+1}=3\underline{P}_n{}^2-2\underline{P}_n{}^3\equiv\underline{\mathcal{P}}_n.\tag{5}$$

Equation (5) has been given by McWeeny[2] for the purpose of "purifying" a nearly idempotent matrix. We now proceed to generalize this result by also imposing physically important constraints on the density matrix $\underline{P}$. Our constrained variational equations are

$$\delta\mathrm{Tr}(\underline{P}^2-\underline{P})^2=0;\quad\mathrm{Tr}\underline{P}\underline{O}_k=O_k,\tag{6}$$

where O_k is the expectation value of the observable $\underline{O}_k$. Formally this problem can be handled by the Lagrangian multiplier technique. Letting $-2\lambda_k$ be the kth Lagrangian multiplier, an equivalent variational problem is

$$\delta \mathrm{Tr}[(\underline{P}^2 - \underline{P})^2 - \textstyle\sum_k 2\lambda_k \underline{P}\,\underline{O}_k] = 0, \tag{7}$$

where the sum is over all the theoretical or experimental constraints to be satisfied.

Proceeding as before, we have to first order

$$\mathrm{Tr}(2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \textstyle\sum_k \lambda_k \underline{O}_k)\delta\underline{P} = 0. \tag{8}$$

Again the arbitrariness of $\delta\underline{P}$ implies that

$$2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \textstyle\sum_k \lambda_k \underline{O}_k = 0. \tag{9}$$

The Lagrange multipliers must now be determined by satisfying the second of Eqs. (6). Just as in the case of the unconstrained equations a solution is most easily obtained iteratively. Thus

$$\underline{P}_{n+1} = \underline{\mathcal{P}}_n + \textstyle\sum_k \lambda_k^{(n)} \underline{O}_k, \tag{10}$$

where $\underline{\mathcal{P}}_n \equiv 3\underline{P}_n^2 - 2\underline{P}_n^3$. In order to determine the Lagrange multipliers at any iteration, one inserts $\underline{P}_{n+1}$ into $\mathrm{Tr}\underline{P}_{n+1}\underline{O}_k = \overline{O}_k$. The λ's then are solutions of the following set of linear inhomogeneous equations,

$$\begin{pmatrix} \mathrm{Tr}\underline{O}_1^2 & \mathrm{Tr}\underline{O}_1\underline{O}_2 & \cdots & \mathrm{Tr}\underline{O}_1\underline{O}_k \\ \vdots & \vdots & & \vdots \\ \mathrm{Tr}\underline{O}_k\underline{O}_1 & \mathrm{Tr}\underline{O}_k\underline{O}_2 & \cdots & \mathrm{Tr}\underline{O}_k^2 \end{pmatrix} \begin{pmatrix} \lambda_1^{(n)} \\ \vdots \\ \lambda_k^{(n)} \end{pmatrix} = \begin{pmatrix} O_1 - \mathrm{Tr}\underline{\mathcal{P}}_n\underline{O}_1 \\ \vdots \\ O_k - \mathrm{Tr}\underline{\mathcal{P}}\,\underline{O}_k \end{pmatrix}. \tag{11}$$

Defining the square matrix on the left of Eq. (11) as $\underline{\tau}$ and the column on the right as $\underline{\Delta}^{(n)}$ then, $\underline{\lambda}^{(n)} \equiv \underline{\tau}^{-1}\underline{\Delta}^{(n)}$.[4] This very simple algorithm has been applied to both heteronuclear diatomic molecules. These applications will be discussed in Secs. V and VII of this paper. In order to study in more detail the variational problem of Eq. (6) we now work to second order in $\delta\underline{P}$ and employ a steepest-descent procedure. Introducing $I \equiv \mathrm{Tr}(\underline{P}^2 - \underline{P})^2$, we have

$$\begin{aligned} \delta(I - 2\textstyle\sum_k \lambda_k \mathrm{Tr}\underline{P}\,\underline{O}_k) &\equiv \mathrm{Tr}[(\underline{P} + \delta\underline{P})^2 \\ &\quad - (\underline{P} + \delta\underline{P})]^2 - I - 2\textstyle\sum_k \lambda_k \mathrm{Tr}\underline{O}_k \delta\underline{P}, \end{aligned} \tag{12}$$

which, after some manipulation, becomes

$$\begin{aligned} &\delta(I - 2\textstyle\sum_k \lambda_k \mathrm{Tr}\underline{P}\,\underline{O}_k) \\ &= 2\mathrm{Tr}(2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \textstyle\sum_k \lambda_k \underline{O}_k)\delta\underline{P} \\ &\quad + \mathrm{Tr}(4\underline{P}^2 - 6\underline{P} + \underline{1})(\delta\underline{P})^2 + 2\,\mathrm{Tr}(\underline{P}\delta\underline{P})^2. \end{aligned} \tag{13}$$

The direction of the descent can now be determined by considering only the first-order term. This term which is of the form $\mathrm{Tr}\underline{A}^\dagger \cdot \underline{B}$ can be considered as a scalar product of two vectors with elements $A_{11} \ldots A_{ij} \ldots$ and $B_{11} \ldots B_{ij} \ldots$ in which case its maximum negative change occurs when $\underline{B} = -\alpha A$. Thus we require that

$$\delta\underline{P} = -\alpha(2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \textstyle\sum_k \lambda_k \underline{O}_k). \tag{14}$$

We now insert Eq. (14) into Eq. (13), and working to second order, we have

$$\begin{aligned} &\delta(I - 2\textstyle\sum_k \lambda_k \mathrm{Tr}\underline{P}\,\underline{O}_k) \\ &= -2\alpha\,\mathrm{Tr}(\underline{P} - \underline{\mathcal{P}} - \textstyle\sum_k \lambda_k \underline{O}_k)^2 \\ &\quad + \alpha^2 \mathrm{Tr}(4\underline{P}^2 - 6\underline{P} + \underline{1})(\underline{P} - \underline{\mathcal{P}} - \textstyle\sum_k \lambda_k \underline{O}_k)^2 \\ &\quad + 2\alpha^2 \mathrm{Tr}[\underline{P}(\underline{P} - \underline{\mathcal{P}} - \textstyle\sum \lambda_k \underline{O}_k)]^2. \end{aligned} \tag{15}$$

We next maximize the variation, or step length, in Eq. (15) by choosing α such that

$$(\partial/\partial\alpha)[\delta(I - 2\textstyle\sum_k \lambda_k \mathrm{Tr}\underline{P}\,\underline{O}_k)] = 0.$$

This yields

$$\alpha = \frac{\mathrm{Tr}\underline{\Delta}^2}{\mathrm{Tr}(4\underline{P}^2 - 6\underline{P} + \underline{1})\underline{\Delta}^2 + 2\,\mathrm{Tr}(\underline{P}\underline{\Delta})^2}, \tag{16}$$

where $\underline{\Delta} \equiv \underline{P} - \underline{\mathcal{P}} - \sum_k \lambda_k \underline{O}_k$.

In the unconstrained problem $\underline{\Delta} = \underline{P} - \underline{\mathcal{P}}$ so that

$$\alpha = \frac{\mathrm{Tr}(\underline{P} - \underline{\mathcal{P}})^2}{\mathrm{Tr}[6(\underline{P}^2 - \underline{P}) + \underline{1}]\,(\underline{P} - \underline{\mathcal{P}})^2}. \tag{17}$$

Now as $(\underline{P}^2 - \underline{P})$ tends to a null matrix, α tends to $+1$. The preceding will be true in the constrained problem also if, in the limit as $\underline{P}$ approaches an idempotent solution, $\lambda_k^{(n)} \to 0$ for all k,[5] more rapidly than $(\underline{P} - \mathcal{P}) \to 0$. In this case Eq. (16) becomes identical to Eq. (17) and again $\alpha \to 1$ so that

$$\underline{P} + \delta\underline{P} \equiv \underline{P} - \alpha[\underline{P} - (\underline{\mathcal{P}} + \textstyle\sum_k \lambda_k \underline{O}_k)] \to \underline{\mathcal{P}} + \textstyle\sum_k \lambda_k \underline{O}_k. \tag{18}$$

Thus Eq. (18) when used iteratively agrees with Eq. (10), i.e.,

$$\underline{P}_n + \delta\underline{P} \equiv \underline{P}_{n+1} = \underline{\mathcal{P}}_n + \textstyle\sum_k \lambda_k^{(n)} \underline{O}_k. \tag{19}$$

We therefore have the result that the steepest-descent method agrees with the first-order method as one nears solution. Given then that both processes converge, only the rate of convergence is different.

In order to use Eq. (14) iteratively, it is necessary to recalculate α at every iteration. This leads to the following steepest-descent iterative equation

$$\underline{P}_n + \delta\underline{P} \equiv \underline{P}_{n+1} = \underline{P}_n - \alpha_n \underline{\Delta}_n. \tag{20}$$

III. NONORTHOGONAL BASES

Equation (20) can easily be transformed to a nonorthogonal basis. Let $\underline{\chi}\equiv\underline{\Psi}\,S^{1/2}$, where $\underline{\Psi}^{\dagger}\cdot\underline{\Psi}=\underline{1}$ (i.e., $\langle\psi_i|\psi_j\rangle=\delta_{ij}$); then $\underline{\chi}^{\dagger}\cdot\underline{\chi}=\underline{S}$ is the metric of the $\underline{\chi}$ basis. One easily shows that the transformed matrix $\underline{O}\equiv\underline{\Psi}^{\dagger}\cdot\hat{O}\underline{\Psi}$ is $\underline{S}^{-1/2}\,\overline{\underline{O}}\,\underline{S}^{-1/2}$, where $\overline{\underline{O}}$ is in the $\underline{\chi}$ basis. In order to complete the transformation, we multiply Eq. (18) on the left by $\underline{S}^{-1/2}$ and the right by $\underline{S}^{1/2}$ and define $\overline{\underline{P}}\equiv\underline{S}^{-1/2}\underline{P}\times\underline{S}^{1/2}$. Then

$$\overline{\underline{P}}_{n+1}=\overline{\underline{P}}_{n}-\alpha_n[\overline{\underline{\varphi}}_n-(\overline{\underline{\varphi}}_n+\textstyle\sum_k\lambda_k^{(n)}\underline{S}^{-1}\overline{\underline{O}}_k)], \tag{21}$$

which is the correct iteration equation for the nonorthogonal basis. Note that the expectation values needed in the constraints are now given by

$$O_k=\mathrm{Tr}\underline{P}\,\underline{O}_k=\mathrm{Tr}\underline{P}\,\underline{S}^{-1/2}\overline{\underline{O}}_k\underline{S}^{-1/2}=\mathrm{Tr}\overline{\underline{P}}\,\overline{\underline{S}}^{-1}\overline{\underline{O}}_k\;. \tag{22}$$

One easily shows also that the steepest-descent parameter α is still given by Eq. (16) except that now

$$\overline{\underline{\Delta}}_n=\overline{\underline{P}}_n-(\overline{\underline{\varphi}}_n+\textstyle\sum_k\lambda_k^{(n)}\underline{S}^{-1}\overline{\underline{O}}_k)\;.$$

The question of convergence we handle in the following operational way. The iteration is carried out until $\underline{P}_{n+1}$ is not changing monotonically (i.e., is randomly oscillating) in the last decimal place and all the λ's have been reduced to zero. This will be discussed in more detail when we consider concrete examples. Practically speaking, we have encountered little difficulty with convergence problems.

IV. THE NUMBER OF CONSTRAINTS REQUIRED TO FIX $\underline{P}$

The question of the number of strictly idempotent solutions of Eq. (9) and the related initial guess problem can be handled in the following way.[6] Recall that idempotency of $\underline{P}=\underline{P}^{\dagger}$ implies factorization. That is, $\underline{P}=\underline{C}\,\underline{C}^{\dagger}$, where $\underline{C}$ is m by N and $\underline{C}^{\dagger}\underline{C}=\underline{1}_N$. The number of essential complex parameters $\kappa(m,N)$ in $\underline{P}$ therefore, is just the number of elements of $\underline{C}$, $m\times N$, less the N^2 normalization and orthogonalization conditions arising from $\underline{C}^{\dagger}\underline{C}=\underline{1}_N$. It follows then, that the number of complex parameters, that have to be fixed in order to determine an Hermitian idempotent $\underline{P}$ matrix with $\mathrm{Tr}\underline{P}=N$, is

$$\kappa(m,N)\equiv m\times N-N^2=N(m-N)\;. \tag{23}$$

In any problem then, where there are exactly $\kappa(m,N)$ independent constraints other than normalization, there is no initial guess problem.[7] On the other hand, suppose we choose a certain class of initial guesses and find that although Eq. (23) is not satisfied; a unique solution results. This implies that we have, with our choice of initial guesses, singled out a portion of the matrix space to which only one solution is accessible. The scalar analog of this idea is easily visualized. For example, only one of the zeros of a function $f(x)$ may be accessible from a given portion of the x axis with a given iteration scheme.

In most of the calculations reported herein the initial $\underline{P}$ matrix $\underline{P}_0$ was based on an atomic or ionic state of the molecule as it would be as $R\to\infty$ (i.e., a separated atom or ion state, ground or excited). This, of course, is a physically interesting class of guesses. Hence it is desirable to ascertain what kinds of solutions are accessible from this separated atom or "ion" portion of $\underline{P}$ space. Some of the dipole-moment results are especially interesting in this regard.

V. LIMITED-BASIS CALCULATION FOR THE MOLECULES C_2, N_2, O_2, AND F_2

We chose to study the molecules C_2, N_2, O_2, and F_2. The reason for this choice is that these molecules all have a similar ground-state electronic configuration. That is, each has six σ_g electrons and four σ_u electrons. They differ therefore only in their π occupation. For a first-row homonuclear molecule with a limited basis, the π part of the density matrix is trivially determined by a knowledge of the total number of such electrons. In the above molecules there are, respectively, two, four, six, and eight electrons. Because of this electronic structure the limited basis calculation reduces to a determination of the 3×3 σ_u block of the $\underline{P}$ matrix, when $\underline{P}$ is referred to a symmetry basis. According to Eq. (23) only two constraints, other than normalization, are necessary. These were chosen to be the experimental electrostatic force and, via the virial theorem, the experimental kinetic energy. The analytical forms of the constraints are

$$\begin{aligned}
&2\mathrm{Tr}\underline{P}\,\underline{S}^{-1}\underline{T}=T_e\equiv T(\infty)+D_e\;,\\
&2\mathrm{Tr}\underline{P}\,\underline{S}^{-1}\underline{F}=Z_AZ_B/R_e^{\,2}\;,\\
&2\mathrm{Tr}\underline{P}=N\;,
\end{aligned}\tag{24}$$

where the factor of 2 is a result of the double occupation of the space part of the molecular orbitals (MO's).

Table I contains the relevant experimental data. Note that $T(\infty)\equiv T_A+T_B$ is somewhat ambiguous, since a variational [best atom (BA)] $T(\infty)$ could just as well be used in Eq. (24) as an experimental $T(\infty)$. We will do both of these calculations and

TABLE I. Experimental constraint data for C_2, N_2, O_2, and F_2.

Molecule	R_e	$T(R_e)_{\mathrm{expt}}$ [a]	$T(R_e)_{\mathrm{BA}}$ [b]
C_2 [c]	2.588	75.424	
N_2	2.074	109.475	108.814
O_2	2.282	150.376	149.271
F_2	2.680	199.572	197.945

[a] $T(R_e)_{\mathrm{expt}}=T(\infty)_{\mathrm{expt}}+D_e$.

[b] $T(R_e)_{\mathrm{BA}}=T(\infty)_{\mathrm{BA}}+D_e$.

[c] The data for carbon are Hartree-Fock data.

give arguments later to indicate that the use of a variational (BA) $T(\infty)$ in the constraint is more consistent theoretically not only with our basic principle [Eq. (2)] but also with the use of the BA basis.

The iterative equations constrained as indicated in Eq. (24) converged always to a unique solution.[7] The convergence criterion used was operational in the sense that iteration proceeded until all elements of the $\underline{P}$ matrix showed no change in the last significant decimal place carried in the calculation. The solution $\underline{P}$ matrix is idempotent to the limit of the number of decimal digits carried in the calculation. In most of the calculations reported here, we worked with eight decimal digits, and our solution λ's were of the order of 10^{-8}.

The results of calculating expectation values using our solution $\underline{P}$ matrices are presented in Table II. We also compare our semiempirical (SE) to limited Hartree-Fock (LHF), Hartree-Fock (HF), and separated atom (SA) expectation values. It is notable first of all that this set of expectation values exhibits very little difference for all calculations ranging from SA to HF. Thus one must be very careful in using these quantities as a measure of the validity of a density matrix. Clearly, just as in the case of the total energy, the effect of molecule formation on these expectation values is a relatively small one. Secondly, we see that our calculations show very little improvement over the separated atom values. It must also be noted, however, that of all the densities referred to in Table II only the HF and our semiempirical, Se, give the correct Hellman-Feynman forces, and of course, only the SE density gives the experimental dissociation energy via the virial theorem. As we will see the latter property is not unambiguously the most desirable.

In the case of N_2 and F_2, Table II also contains calculations for a density derived from the alternate kinetic-energy constraint referred to above. Thus

$$2\,\mathrm{Tr}\underline{\underline{P}}\,\underline{\underline{S}}^{-1}\underline{T} = T(\infty)_{BA} + D_e\,, \qquad (25)$$

where $T(\infty)_{BA}$ is the best-atom variational energy. It appears that this constraint is more nearly consistent theoretically with the idempotency or single-configuration representability of our density. The reason for this is the following: Our solution $\underline{P}$ matrices imply N-body single configuration wave functions. The energy variational theorem then requires that if we used this function to calculate $\langle \hat{H} \rangle$[8] we would find that $\langle \hat{H} \rangle > U_{\mathrm{expt}}$. But our virial-theorem constraint of Eq. (24) requires that $\langle \hat{T} \rangle = T_{\mathrm{expt}} \equiv -U_{\mathrm{expt}}$. Clearly then, our calculated kinetic and total energies can never be consistent, because by virtue of the previous expressions $-\langle \hat{T} \rangle < \langle \hat{H} \rangle$. Thus an inconsistency exists when $T(\infty)_{\mathrm{expt}}$ is used. On the other hand, this inconsistency is lessened in the constraint of Eq. (25). The reason for this is that we are not now forcing an idempotent $\underline{P}$ matrix to take up the full correlation kinetic energy but only that involved in the dissociation energy. Thus Eq. (25) is much more nearly a *bona fide* Hartree-Fock constraint.

Another reason for using $T(\infty)_{BA}$ is that it more nearly corresponds to the best-atom basis used to represent the densities. Indeed if we did the calculation as $R \to \infty$, $T(\infty)_{BA}$ would become a *bona fide* limited Hartree-Fock constraint.

VI. THE CONNECTION BETWEEN THE PRESENT METHOD AND THE HARTREE-FOCK METHOD

The final homonuclear calculation to be discussed is one that corroborates a theorem alluded to in the introduction. In brief, this theorem establishes

TABLE II. Expectation-value comparison for $T(R_e)_{\mathrm{expt}}$ and $T(R_e)_{\mathrm{BA}}$ calculations.

Molecule	Method	$\langle r_A^2 \rangle$	$\langle z_A^2 \rangle$	$\langle 1/r_A \rangle$	$\langle \xi \rangle$
C_2	SE	65.838	50.083	16.961	18.653
	HF[a]	68.875	52.199	16.978	18.938
	SA	64.349	48.232	16.821	18.475
N_2	SE $[T(R_e)_{\mathrm{expt}}]$	49.729	35.524	21.673	22.199
	$[T(R_e)_{\mathrm{BA}}]$	50.538	36.276	21.607	22.371
	LHF[b]	52.970	38.920	21.480	22.830
	HF	54.180	38.762	21.646	22.873
	SA	50.547	36.798	21.477	22.333
O_2	SE	59.897	48.548	23.348	25.768
	HF[a]	64.182	49.354	24.137	25.692
	SA	59.915	47.745	23.398	25.513
F_2	SE $[T(R_e)_{\mathrm{expt}}]$	81.102	70.430	24.157	29.888
	$[T(R_e)_{\mathrm{BA}}]$	82.596	71.914	24.067	29.771
	LHF	81.865	69.810	24.321	29.799
	HF	86.335	71.475	24.775	
	SA	80.899	70.061	24.127	29.597

[a] P. Cade, University of Chicago, private communication.

[b] B. Ransil, Rev. Mod. Phys. 32, 239 (1960).

the connection between the present method and any limited Hartree-Fock calculation done with the same basis.

The theorem can be most precisely stated by first defining a variational problem. This is done by setting down the extremum condition and the constraints. We have

$$\delta\,\mathrm{Tr}(\underline{P}^2-\underline{P})^2=0,\quad \mathrm{Tr}\underline{P}=N,\quad \mathrm{Tr}\underline{P}\,\underline{O}_k=O_k,$$
$$k=1,\cdot\cdot\cdot,\quad \kappa(m,N),\qquad(26)$$

where $\underline{O}_k$ is an m-square matrix representative of an operator in the m-basis $\underline{\Psi}$ and O_k is a *bona fide* limited Hartree-Fock expectation value. With the variational problem defined, we now state the theorem. One of the idempotent solutions of Eqs. (26) is the limited Hartree-Fock density matrix $\underline{P}_{\mathrm{HF}}$ provided the constraints of Eq. (26) are computed with $\underline{P}_{\mathrm{HF}}$ (this is what we mean by a *bona fide* Hartree-Fock constraint). The proof of this theorem is simple. Thus the class of all m-square, Hermitian, idempotent $\underline{P}$ matrices contains the corresponding m-basis limited Hartree-Fock $\underline{P}_{\mathrm{HF}}$. But such a matrix requires only a finite number $\kappa(m,N)$ of constraints to determine it. If therefore $\mathrm{Tr}\underline{P}\,\underline{O}_k=O_k$, $k=1\cdot\cdot\cdot\kappa(m,N)$ are *bona fide* limited Hartree-Fock constraints, one of the idempotent solutions of Eq. (26) must be the corresponding limited Hartree-Fock $\underline{P}_{\mathrm{HF}}$ matrix.

Numerical corroboration of this theorem is given by the following calculations. For the molecules N_2 and F_2 the $\underline{P}_{\sigma_u}$ matrix is completely determined by two constraints other than normalization. We chose these to be kinetic energy and force and used the actual calculated limited Hartree-Fock values[9] as our constraints. In both N_2 and F_2, the corresponding limited Hartree-Fock matrix was exactly reproduced independent of our initial guess.

It is manifest that the previous considerations are much more generally applicable, that, is *any* pure state can be selected out of the class of all Hermitian idempotent matrices with a sufficient set of the pure-state expectation values.

VII. APPLICATION TO HETERONUCLEAR MOLECULES

Because of the availability of experimental and Hartree-Fock[10] dipole moments, we chose to study the series of molecules FH, OH, NH, LiH, LiF, and BF.[11] The pertinent experimental data are given in Table III.

TABLE III. Heteronuclear experimental data (a.u.).

Molecule	R_e	$T(R_e)_{\mathrm{expt}}$
FH	1.733	100.53
OH	1.834	75.78
NH	1.976	55.53
LiH	3.015	8.07
LiF	2.850	107.50
BF	2.385	124.74

Using Eq. (23) one easily sees that the hydride $\underline{P}$ matrices can be determined with the three constraints F_A, F_B, and T when a four-function σ basis is used. In the case of LiF and BF a ten-function (limited) basis is used. Whenever results are reported for a case in which Eq. (23) is not satisfied, the initial guess will be given with some explanation.

As in the case of the homonuclear molecules, we made calculations with both $T(\infty)_{\mathrm{expt}}$ and $T(\infty)_{BA}$ – here for two reasons. First, we are interested in the importance of the effect of the energy inconsistency referred to in Sec. V and, in particular, with reference to dipole moments. Second, this calculation gave an idea of how the dipole moment varies with the T constraint and, therefore, how sensitive it is to errors in the dissociation energy.

Table IV displays the two sets of calculated dipole moments compared to experimental (LHF) and (HF) values. It, first of all, is to be noted that $|\mu|$ is in some cases very sensitive to a change in the energy constraint – a 1% change in T of the hydrogen fluoride molecule, for example, inducing a 30% change in the net dipole moment. This is not as serious as it might at first seem, however, since errors in the dissociation energy are generally only of the order of 0.05% (or usually much less) of the total energy, and therefore one should not expect these errors to cause more than about 1% lack of precision in $|\mu|$. At present, of course, errors of this order are not our most serious problem.

The next thing we note about the dipole moments is that they were very poor for all LiH calculations made with a six function basis no matter what ini-

TABLE IV. Dipole-moment comparison (debye units).

Molecule (– +)	μ_{SE}				
	$T(\infty)_{\mathrm{BA}}$	$T(\infty)_{\mathrm{expt}}$	μ_{HF}	μ_{LHF}	μ_{expt}
FH	2.21	1.75	1.98	1.12	1.82
OH	2.29	1.88	1.78		1.65
NH	2.27	1.93	1.93/1.63	1.68	
LiH[a]	−5.82	−6.17	−6.00	−6.48	−5.88
LiF[b]	−6.70	−6.70	−5.86	−3.43	−6.28
BF[c]	−0.584	−0.687	−0.668	−1.96	

[a] 10 function basis. [b] Charge-transfer guess. [c] Atomic guess.

TABLE V. LiH dipole moments and initial guesses. The guess is designated by the atomic occupation numbers, e.g., the ground state is given by (2101) referred to $1S_{\mathrm{Li}}$, $2S_{\mathrm{Li}}$, $2P_{\mathrm{Li}}$, and $1S_{\mathrm{H}}$.

Guess	Dipole moment	Character of the guess
(2 1 0 1)	−1.36	Ground atomic state
$(2\ \frac{1}{2}\ 0\ \frac{3}{2})$	−5.41	Partial charge transfer
(2 0 0 2)	−6.17	Charge transfer

TABLE VI. Hellmann-Feynman electronic-force comparison (a.u.).

Molecule	LHF F_A	LHF F_B	Experimental $F_A = F_B$
FH	3.438	2.859	2.997
NH	2.326	1.743	1.793
LiH	0.487	0.272	0.330
LiF	3.463	2.060	3.092
BF	7.093	4.873	7.911
N_2	9.422	9.422	11.462
F_2	9.468	9.468	11.015

tial guess was used. This led us to try a calculation in which additional basis functions were introduced on the hydrogen atom. The reasoning involved here is that LiH is well known to be a charge-transfer type molecule, i.e., $\mathrm{Li}^+\mathrm{H}^-$, and therefore a single 1*s* function on hydrogen is not capable of handling this transfer in addition to all of the other conditions. The rectitude of this reasoning seems to be borne out by the excellent dipole moments that resulted when we used a charge transfer guess (see Table V).

We would like to emphasize at this point that although there seem to be some regularities in the deviation of the dipole moments from experimental values, the present calculations are to be viewed as interim in nature and certainly to be improved as more constraints are included. Our results should be compared with limited Hartree-Fock (LHF), which is the nonempirical analog of our calculation. In this connection, we make note of the LHF Hellman-Feyman forces. Table VI contains these data. In general, the LHF forces are very poor, and more often than not, our calculated dipole moments are better.

VIII. CONCLUSION

It is to be noted in conclusion that all the results herein reported have been obtained with what is usually called a limited best-atom basis. Insofar as our dipole-moment results are generally an improvement over limited-basis variational calculations, our method must be considered a better "fitting" procedure for the first-order density. Thus a "best fit" of the Hartree-Fock density to a limited basis (at least as far as $|\mu|$ is concerned) is more nearly achieved using the method presented in this paper than by energy minimization techniques. (See paper IV for a more detailed analysis of this "fitting" aspect of the $\underline{P}$ equations.)

The prognosis for polyatomics seems to be very good. This conclusion depends upon the assumption that the densities we calculate can only improve with the addition of more constraints, and upon the fact that all of our results have been obtained using relatively modest computational facilities, which leaves open the full exploitation of large machines for polyatomic molecules.

A final point that should be made is that the method is open to the incorporation of possibly many other constraints via the theory of the hypervirials[12] and local energies.[13] It is well known that both of these methods offer, in principle, a way of completely determining the wave function of a many-body system. Unfortunately, no one has as yet invented a computationally smooth way of doing this. One of the possible future developments in our method could be in this direction.

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[1] W. L. Clinton, J. Nakhleh and F. Wunderlich, Phys. Rev. 177, 1 (1969); paper I of this series, preceeding paper.

[2] R. McWeeny, Rev. Mod. Phys. 32, 335 (1960).

[3] An alternate proof proceeds as follows: if $\underline{P} = \underline{P}^\dagger$ then

$$\mathrm{Tr}(\underline{P}^2 - \underline{P})^2 = \sum_{i,j} |(\underline{P}^2 - \underline{P})_{ij}|^2,$$

and is zero if and only if $\underline{P}^2 = \underline{P}$.

[4] We note that at solution the Lagrange multipliers λ_k must vanish; i.e.,

$$\lim_{n\to\infty} \lambda_k^{(n)} = 0 \text{ for all } k.$$

This is evident because $\underline{\tau}$ is nonsingular and at solution $\mathcal{P} = \underline{P}$, and therefore, $\underline{\Delta}$ is a null vector.

[5] It is not at present clear what conditions ensure that the λ_k vanish more rapidly than $\underline{P} - \underline{\mathcal{P}}$.

[6] A similar proof is given by P. Roman Advanced Quantum Theory (Addison-Wesley Publishing Co. Inc., Reading, Mass., 1965), p. 96. It should be noted that Roman's equation refers to the number of real parameters in an idempotent matrix of rank one.

[7] However, because the conditions on the elements of $\underline{C}$ are bilinear, several solutions are possible. Any solution generated, however, will have the desired properties of idempotency and constraint satisfaction. In the present work we have had no difficulty with multiple solutions.

[8] $$H \equiv -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|}$$

$$+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|}+\frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha-\vec{R}_\beta|}.$$

[9] B. Ransil, Rev. Mod. Phys. 32, 239 (1960).

[10] P. Cade, University of Chicago, (private communication).

[11] There are dipole-moment data available on still other heteronuclear molecules. Our preliminary results for BH, CH, and CO, however, indicate that force and kinetic energy are not effective in yielding good dipole moments. These molecules are in a different class than the ones we report, in that they are generally considered to be more covalent in nature. There seems to be some significance to this, but any detailed analysis at the present time would be premature.

[12] J. O. Hirshfelder, J. Chem. Phys. 33, 1462 (1960).

[13] A. A. Frost, Rev. Mod. Phys. 32, 313 (1960).

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Direct Determination of Pure-State Density Matrices. III. Purely Theoretical Densities Via an Electrostatic-Virial Theorem*

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A combined electrostatic virial theorem is introduced and used to derive a differential equation for the scale factor ζ in a diatomic molecule. This equation can either be used to compute $d\zeta/dR$ or it can be integrated to yield

$$\zeta(\overline{R})=\left(\frac{T(\overline{R}_0)}{T(\overline{R})}\right)^{1/2}\left(\zeta(\overline{R}_0)-\frac{1}{2T(\overline{R}_0)}\int_{\overline{R}}^{\overline{R}_0}\frac{2F(R)-RdF(R)/dR}{T(R)^{1/2}}\,dR\right),$$

where R is the internuclear distance, $\overline{R}\equiv\zeta R$, $F=\langle-\partial V_1/\partial R\rangle$, with V_1 the one-electron potential, $T\equiv\langle\sum_i-\frac{1}{2}\nabla_i^2\rangle$, and $\overline{R}_0$ is an integration limit. It is shown that if $\zeta(\overline{R}_0)$ is a variational scale factor, then $\zeta(\overline{R})$ is also a variational scale factor provided the electron density ρ_1 involves no other unoptomized variational parameters. Unlike the conventional variational expression for ζ, which contains two-electron integrals, the above formula involves only the one-electron force and kinetic energy integrals. Using this ζ, electron densities and energies are calculated for $H_2{}^+$, H_2, He_2, and Li_2 and compared with experimental and variationally calculated values. Qualitative agreement is obtained in general, and, in particular, our theoretical energy curve for He_2 is in very good agreement with the best variational results for 1.5 a.u. $<R<\infty$. It is also shown how the electrostatic-virial theorem can be used as a condition in continuing density-matirx calculations from R to $R+\Delta R$.

I. INTRODUCTION

In the first paper in this series,[1] the electrostatic and virial theorems were used to determine a semiempirical electron density. The method consisted of three main steps: (a) A simple functional form for $\rho_1(\vec{r}\,',\vec{r},R)$ was assumed and inserted into the electrostatic and virial theorems. (b) In place of the electronic energy E(R) and its derivative $dE(R)/dR$, experimental data were used. (c) The resulting equations, which by virtue of (a) and (b) uniquely determine ρ_1, were solved.

In the present paper, a similar approach is followed except that the semiempirical aspect [step (b) above] is eliminated. This is accomplished by combining the electrostatic and virial theorems into a single equation that can be expressed entirely in terms of the one-body density $\rho_1(\vec{r}\,',\vec{r},R)$. This electrostatic-virial (EV) theorem can then be used as a purely theoretical condition on the one-body density.

If the density is expressed as $\rho_1=\zeta^3\rho_1(\zeta\vec{r}\,',\zeta\vec{r},\zeta R)$, the EV theorem serves to uniquely determine ζ in terms of force and kinetic-energy integrals involving only the unscaled density $\rho_1(\vec{r}\,', \vec{r}, R)$. In the first parts of this paper, a method is developed for the theoretical calculation of the scale factor ζ. It is shown that our ζ is the same as the variational scale factor provided the density contains no other unoptimized variational parameters. It is also shown computationally that, even though many of the densities we work with do contain other unoptimized variational parameters, our ζ's are, in every case, in qualitative agreement with the variational ζ's, and in one important case quantitative agreement is obtained.

The last part of the present paper is devoted to the derivation of density-matrix equations that allow one to continue an idempotent matrix from one value of a parameter λ to another $\lambda+\Delta\lambda$.