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Direct Determination of Pure-State Density Matrices. IV. Investigation of Another Constraint and Another Application of the $\underline{P}$ Equations *

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An additional theorem of the Hellman-Feynman variety is used in conjunction with the equations derived in paper II for the first-order density matrix. This particular theorem due to Parr relates the energy difference $E(\lambda')-E(\lambda)$ to a "parameter-transition density" $\rho(\lambda',\lambda)$. It is shown that $E(\lambda')-E(\lambda)$ can be used as a constraint on either $\rho(\lambda')$ or $\rho(\lambda)$. An additional application of the $\underline{P}$ equations as a density-fitting technique is investigated. That is, given a set of expectation values in some basis $\underline{\Psi}$, one can use the $\underline{P}$ equations to generate the density matrix that corresponds to these expectation values in some other basis $\underline{\chi}$. Several helium-atom Hartree-Fock densities are fitted to smaller bases with various sets of operators. Density graphs are given for comparison.

I. INTRODUCTION

In a previous paper[1] in this series, a constrained idempotency variational condition was applied to the first-order density matrix. The variational problem gave rise to an iterative matrix equation. It was shown there that the main difficulty was the lack of sufficient conditions to fully constrain the density matrix. It was also shown that when *bona fide* Hartree-Fock constraints were used to fully constrain a problem, the corresponding Hartree-Fock density matrix was uniquely generated.

In this paper, we consider the use of additional Hellman-Feynman-type theorems as constraints In particular, the Hellman-Feynman theorem for dE/dZ is studied where Z is the nuclear charge. Because of inherent inaccuracies in computing numerical derivatives with a finite amount of energy data, the dE/dZ expression is, in general, not useful as an experimental constraint. Also, since the Hellman-Feynman theorem applies only to $(\partial E/\partial Z)_N$ (where N is the number of electrons), isoelectronic energy data are necessary. However, the available data are usually not sufficiently complete to compute reliable numerical derivatives.

However, on the positive side, we have made use of a theorem due to Parr[2] which relates $E(\lambda')-E(\lambda)$ to a one-body "parameter-transition density." Here λ is any parameter of the system not entering into the two-body part of the Hamiltonian. Although Parr's theorem applies only to exact wave functions, we will show by direct computation that it is very accurately fulfilled in, for example, two-electron atomic Hartree-Fock densities. At least in these cases, then, the ΔE theorem is a *bona fide* Hartree-Fock constraint.

The density matrix formalism for ΔE is worked out in Sec. III, where it is shown that the "parameter-transition density matrix" can be written in terms of the density matrices $\underline{P}(\lambda')$ and $\underline{P}(\lambda)$. The ΔE theorem then fits nicely into our method. In Sec. V, we apply the formalism to some two-electron self-consistent-field (SCF) densities.

In Sec. IV, we combine ΔE and the electrostatic theorem to produce a purely theoretical transition constraint on the first-order density.

In Sec. V, the atomic Hartree-Fock densities are used to further corroborate some of the results of paper II. In particular, we numerically test the theorem that the fully constrained $\underline{P}$ equations will generate the proper n-basis pure-state density matrix. Obviously, the constraints used must correspond to the state in question. One of the important aspects of this theorem is the fact that if a sufficient number of *bona fide* Hartree-Fock constraints can be found, then the strictly idempotent solutions of our equations are true Hartree-Fock density matrices.

In Sec. VI, using the same two-electron SCF densities, an additional application of the idempotency equations is discussed. It is shown that a given set of expectation values in some basis is sufficient to determine a "fit" of the corresponding density in some other basis. Although not a least-squares-type fit, it is shown to have considerable numerical advantages.

II. THE HELLMAN-FEYNMAN THEOREM FOR Z

In this part we discuss in more detail the difficulties with dE/dZ. Thus consider an N-electron molecular system with energy $E(\vec{R}_\alpha \ldots \vec{R}_\nu, Z_\alpha \ldots Z_\nu, N)$, where $\vec{R}_\alpha$ and Z_α are the αth nuclear position vector and charge. Then, using

$$dE=\sum_\alpha \frac{\partial E}{\partial Z_\alpha}\,dZ_\alpha+\sum_\alpha \vec{\nabla}_\alpha E\cdot d\vec{R}_\alpha+\frac{\partial E}{\partial N},$$

we have

$$dE=\sum_\alpha\left(\int-\frac{1}{|\vec{r}-\vec{R}_\alpha|}\,\rho_1 d^3r\right)dZ_\alpha +\sum_\alpha\left[\int\vec{\nabla}_\alpha\left(\frac{-Z_\alpha}{|\vec{r}-\vec{R}_\alpha|}\right)\rho_1 d^3r\right]\cdot d\vec{R}_\alpha+\frac{\partial E}{\partial N}\,dN, \quad (1)$$

since by the Hellman-Feynman theorem

$$\partial E(\lambda,\cdots)/\partial\lambda_n=\langle\partial H/\partial\lambda_n\rangle,$$

so that

$$\frac{\partial E}{\partial Z_\alpha}=\int\left(-\frac{1}{|\vec{r}-\vec{R}_\alpha|}\right)\rho_1 d^3r;$$

$$\vec{\nabla}_\alpha E = \int \vec{\nabla}_\alpha \left(\frac{-Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \right) \rho_1 d^3 r. \tag{2}$$

Even though $Z_\alpha \ldots Z_\nu$ and N are discrete variables, Eq. (1) is, in principle, legitimate since we can always think of some continuous function that passes through the discrete points defined by E; actually, an infinite number of such functions exist. This is one of the difficulties; since only a discrete set of experimental numbers is available, an empirical evaluation of dE/dZ is unreliable. Thus, if we want to use Eq. (1) as a constraint in the usual way, we have to be content with the inherent inaccuracy in a numerical derivative determined from a discrete set of data points.

Another difficulty with Eq. (1) is the term $\partial E/\partial N$. Unfortunately, there is no Hellman-Feynman analog for this quantity, since N is not the kind of parameter considered in this theorem. Thus, if $|N\rangle$ is the many-body state vector, $\partial |N\rangle/\partial N$ is not easy to define. The same difficulty is encountered with the derivative of the many-body Hamiltonian. On the other hand, we could use the quantity $\partial E/\partial N$ as an experimental number. Again, however, we encounter inaccurate numerical derivatives, not to mention the fact that data such as $\Delta E/\Delta N$, holding Z fixed, are not readily available.

For these reasons, then, the Hellman-Feynman theorem for dE/dZ has, for now, been discarded as a possible experimental constraint.

III. PARR'S THEOREM IN DENSITY MATRIX FORM

The finite difference analog of the Hellman-Feynman Theorem has been given by Parr.[2] He showed that

$$\begin{aligned} \Delta E &= E(\lambda') - E(\lambda) \\ &= \int [\hat{H}(\lambda') - \hat{H}(\lambda)] \rho_1(\lambda', \lambda) d^3r / \langle \lambda', \lambda \rangle \end{aligned} \tag{3}$$

where λ is some parameter entering into the one-body part of the Hamiltonian with state vector $|\lambda\rangle$, representative $\Psi(\lambda)$, and parameter-transition density $\rho_1(\lambda'\lambda) \equiv N\int \Psi^*(\lambda')\Psi(\lambda) d^3r_2 \ldots d^3r_N$. The one-body parameter-transition density will be referred to as the transition density.

As we will show, Eq. (3) is well satisfied for two-electron atomic Hartree-Fock transition densities when λ is the nuclear charge. In order to do this calculation and also for application in our general program, we need a density matrix form for Eq. (3).

Consider two sets of Hartree-Fock functions for an N-body system;

$$\underline{\Phi}(\lambda) = \underline{\Psi}(\lambda)\underline{C}(\lambda); \quad \underline{\Phi}(\lambda') = \underline{\Psi}(\lambda')\underline{C}(\lambda')$$

where $\Psi(\lambda)$ is some m basis with metric

$$\underline{S}(\lambda) \equiv \underline{\Psi}^\dagger(\lambda) \circ \underline{\Psi}(\lambda).$$

The symbolic product is defined via

$$S_{ij} \equiv \Psi_i^\dagger \cdot \Psi_j = \langle \psi_i | \psi_j \rangle .$$

As usual we have

$$\underline{R} = \underline{C}\,\underline{C}^\dagger; \quad \underline{P} = \underline{R}\,\underline{S}; \quad \underline{P}^2 = \underline{P}; \quad 2\,\mathrm{Tr}\underline{P} = N \tag{4}$$

for either λ or λ'. Now define

$$\underline{\mathfrak{s}}(\lambda', \lambda) \equiv \underline{\Phi}^\dagger(\lambda') \circ \underline{\Phi}(\lambda);$$

then introduce new functions

$$\underline{\chi}(\lambda) = \underline{\Phi}(\lambda)\underline{\mathfrak{s}}^{-1/2}(\lambda', \lambda)$$

and $\underline{\chi}(\lambda') \equiv \underline{\Phi}(\lambda')\underline{\mathfrak{s}}^{-1/2\dagger}(\lambda', \lambda)$.

Clearly, we have

$$\underline{\chi}(\lambda')^\dagger \cdot \underline{\chi}(\lambda) = \underline{1}$$

provided $\underline{\mathfrak{s}}^{-1/2}(\lambda', \lambda)$ exists. One can then easily show that the transition density is given by

$$\begin{aligned} \rho_1(\lambda', \lambda)/\langle \lambda' | \lambda \rangle &= 2\,\mathrm{Tr}\,\underline{\chi}^\dagger(\lambda')\underline{\chi}(\lambda) \\ &= 2\,\mathrm{Tr}\underline{\mathfrak{s}}^{-1}(\lambda', \lambda)\underline{\Phi}^\dagger(\lambda')\underline{\Phi}(\lambda). \end{aligned} \tag{5}$$

The second expression in Eq. (5) has the same formal appearance as an ordinary Hartree-Fock density, which is obtained by setting $\lambda' = \lambda$. Equation (5) can now be expressed in terms of the $\underline{\Psi}$ basis by defining

$$\underline{S}(\lambda', \lambda) \equiv \underline{\Psi}^\dagger(\lambda') \cdot \underline{\Psi}(\lambda).$$

Thus we see that

$$\begin{aligned} \frac{\rho_1(\lambda', \lambda)}{\langle \lambda' | \lambda \rangle} &= 2\,\mathrm{Tr}\underline{C}(\lambda)[\underline{C}^\dagger(\lambda')\,\underline{S}(\lambda', \lambda)\underline{C}(\lambda)]^{-1} \\ &\quad \times \underline{C}^\dagger(\lambda')\underline{\Psi}^\dagger(\lambda')\underline{\Psi}(\lambda). \end{aligned} \tag{6}$$

We now introduce transition density and transition population matrices via

$$\underline{R}(\lambda', \lambda) = \underline{C}(\lambda)[\underline{C}^\dagger(\lambda')\underline{S}(\lambda', \lambda)\underline{C}(\lambda)]^{-1}\underline{C}^\dagger(\lambda'), \tag{7}$$

$$\underline{P}(\lambda', \lambda) \equiv \underline{R}(\lambda', \lambda)\underline{S}(\lambda', \lambda).$$

Using Eqs. (6) and (7), it then follows from Eq. (3) that

$$\Delta E = 2\,\mathrm{Tr}\underline{P}(\lambda', \lambda)\underline{S}^{-1}(\lambda', \lambda)\Delta\underline{H}(\lambda', \lambda),$$

where $(\Delta\underline{H})_{ij} \equiv \int \psi_i^*(\lambda')[\hat{H}(\lambda') - \hat{H}(\lambda)]\psi_j(\lambda) d^3r.$

From Eqs. (7) it follows that

$$\underline{R}(\lambda', \lambda)\underline{S}(\lambda', \lambda)\underline{R}(\lambda', \lambda) = \underline{R}(\lambda', \lambda);$$

$$\underline{P}(\lambda', \lambda)\underline{P}(\lambda', \lambda) = \underline{P}(\lambda', \lambda). \tag{8}$$

Since $\underline{C}(\lambda)$ and $\underline{C}(\lambda')$ are the rectangular matrices of occupied eigenvectors of $\underline{P}(\lambda)$ and $\underline{P}(\lambda')$, then it follows that[1]

$$\underline{P}(\lambda)\underline{C}(\lambda) = \underline{C}(\lambda); \quad \underline{P}(\lambda')\underline{C}(\lambda') = \underline{C}(\lambda') \tag{9a}$$

while from Eqs. (7) it follows that

$$\underline{P}(\lambda,\lambda')\underline{C}(\lambda')=\underline{C}(\lambda');\quad \underline{P}(\lambda',\lambda)\underline{C}(\lambda)=\underline{C}(\lambda). \tag{9b}$$

Again we note the formal similarity between transition and ordinary Hartree-Fock population matrices. Equations (9) also supply some coupling conditions. These are,

$$\underline{P}(\lambda',\lambda)\underline{P}(\lambda)=\underline{P}(\lambda);\quad \underline{P}(\lambda,\lambda')\underline{P}(\lambda')=\underline{P}(\lambda'). \tag{10}$$

In our method, we do not use all of the previous conditions. They are included here only for completeness.

The way in which we introduce ΔE as a constraint depends upon the fact that the transition matrix $P(\lambda',\lambda)$ can always be represented in terms of the "pure" matrices $\underline{P}(\lambda)$ and $\underline{P}(\lambda')$. We now proceed to prove this. For simplicity the derivation will be given for orthogonal bases [i.e., $\underline{S}(\lambda)\equiv\underline{S}(\lambda')=\underline{1}$].

From Eq. (9a) and the idempotency of $\underline{P}(\lambda)$ and $\underline{P}(\lambda')$ we can write

$$\underline{C}(\lambda)=\underline{P}_{N/2}(\lambda)\underline{\alpha}(\lambda),\quad \underline{C}(\lambda')=\underline{P}_{N/2}(\lambda')\underline{\alpha}(\lambda') \tag{11}$$

as can easily be seen by substituting Eq. (11) into Eq. (9a). Here $\underline{P}_{N/2}$ denotes any $N/2$ columns of $\underline{P}$ and $\underline{\alpha}$ is an $N/2$ square matrix to be chosen such that $\underline{C}^\dagger\underline{C}=\underline{1}$. When $N=2$, $\underline{C}$ is simply a column vector and Eq. (11) states that $\underline{C}$ is proportional to any arbitrary column of $\underline{P}$. In the more general case, if one chooses $\underline{\alpha}\equiv(\underline{P}_{N/2}{}^\dagger\underline{P}_{N/2})^{-1/2}$ the orthonormalization condition on $\underline{C}$ will automatically be satisfied; i.e., $\underline{C}^\dagger\underline{C}=\underline{1}$. Since $\underline{P}_{N/2}{}^\dagger\times\underline{P}_{N/2}$ is Hermitian and thus diagonalizable, $(\underline{P}_{N/2}{}^\dagger\underline{P}_{N/2})^{1/2}$ can always be constructed; in addition, by requiring that $\underline{P}_{N/2}{}^\dagger\underline{P}_{N/2}$ be nonsingular the existence of $\underline{\alpha}$ is ensured.

We now insert Eqs. (11) into the definition of $\underline{R}(\lambda',\lambda)$ and observe that

$$\underline{R}(\lambda',\lambda)=\underline{P}_{N/2}(\lambda)\underline{\alpha}(\lambda)[\underline{\alpha}(\lambda')\underline{P}_{N/2}{}^\dagger(\lambda')\times\underline{S}(\lambda',\lambda)\underline{P}_{N/2}(\lambda)\underline{\alpha}(\lambda)]^{-1}\underline{\alpha}(\lambda')\underline{P}_{N/2}{}^\dagger(\lambda'). \tag{12}$$

But clearly (we have used the fact that $\underline{\alpha}=\underline{\alpha}^\dagger$) the square matrices $\underline{\alpha}(\lambda)$ and $\underline{\alpha}(\lambda')$ cancel out of this expression, so that

$$\underline{R}(\lambda',\lambda)=\underline{P}_{N/2}(\lambda)[\underline{P}_{N/2}{}^\dagger(\lambda')\times\underline{S}(\lambda',\lambda)\underline{P}_{N/2}(\lambda)]^{-1}\underline{P}_{N/2}(\lambda'). \tag{13}$$

Using Eq. (13) we can now included any parameter-transition constraint into our regular variational procedure.[1] To do this most simply, we need to write $\underline{P}_{N/2}$ in terms of the full m-square $\underline{P}$ matrix. Since $\underline{P}^2=\underline{P}$ and $\mathrm{Tr}\underline{P}=N/2$ it follows that $\underline{P}$ is of rank $N/2$; i.e., it has only $N/2$ linearly independent columns. Thus, in constructing $\underline{\alpha}$ some caution must be exercised in selecting from the set of m columns of $\underline{P}$ a linearly independent $N/2$ subset. However, since for our present purposes we do not need $\underline{\alpha}$ as such, we may let

$$\underline{P}_{N/2}=\underline{P}\underline{\eta} \tag{14}$$

where $\underline{\eta}$ is $m\times N/2$ and selects from $\underline{P}$ the $N/2$ linearly independent columns.[3]

We now have for $\underline{R}(\lambda',\lambda)$ the following expression:

$$\underline{R}(\lambda',\lambda)=\underline{P}(\lambda)\underline{\eta}\{[\underline{P}(\lambda')\underline{\eta}]^\dagger\times\underline{S}(\lambda',\lambda)\underline{P}(\lambda)\underline{\eta}\}^{-1}[\underline{P}(\lambda')\underline{\eta}]^\dagger. \tag{15}$$

Now we can introduce any constraining condition[1] involving $\underline{R}(\lambda',\lambda)$ into our ordinary variational method without difficulty since $\underline{\eta}$ suffers no variation. Thus, a transition constraint would take the form

$$\Delta E=2\,\mathrm{Tr}\underline{P}(\lambda)\underline{\eta}\{[\underline{P}(\lambda')\underline{\eta}]^\dagger\times\underline{S}(\lambda',\lambda)\underline{P}(\lambda)\underline{\eta}\}^{-1}[\underline{P}(\lambda')\underline{\eta}]^\dagger\Delta\underline{H}(\lambda',\lambda). \tag{16}$$

IV. TRANSITION CONSTRAINTS OF THE *P* MATRIX

In general, the term

$$\{[\underline{P}(\lambda')\underline{\eta}]^\dagger\underline{S}(\lambda',\lambda)\underline{P}(\lambda)\underline{\eta}\}^{-1},$$

which occurs in Eq. (15), is a square matrix of dimension $N/2$. We see, then, that if $N=2$ this quantity is a scalar and can be removed from the trace in Eq. (16). Thus for $N=2$

$$2\,\mathrm{Tr}\underline{P}(\lambda)\underline{\eta}[\underline{P}(\lambda')\underline{\eta}]^\dagger\Delta\underline{H}=\Delta E\{[\underline{P}(\lambda')\underline{\eta}]^\dagger\underline{S}(\lambda',\lambda)\underline{P}(\lambda)\underline{\eta}\} \tag{17}$$

is an alternative form of the transition constraint. But, any scalar can be written as a trace, so we also have

$$\mathrm{Tr}\underline{P}(\lambda)\underline{\eta}\,\underline{\eta}^\dagger\underline{P}^\dagger(\lambda')\Delta\underline{H}=\tfrac{1}{2}\Delta E\,\mathrm{Tr}\underline{P}(\lambda)\underline{\eta}\,\underline{\eta}^\dagger\underline{P}^\dagger(\lambda')\underline{S}(\lambda',\lambda) \tag{18}$$

or

$$\mathrm{Tr}\underline{P}(\lambda)\underline{\eta}\,\underline{\eta}^\dagger\underline{P}^\dagger(\lambda')[\Delta\underline{H}-\tfrac{1}{2}\Delta E\underline{S}(\lambda',\lambda)]=0. \tag{19}$$

This constraint can now be included in a normal way into our variational problem since when we vary $\underline{P}(\lambda)$ we suppose that $\underline{P}(\lambda')$ is being held fixed. Thus if we define

$$\underline{O}_t\equiv\underline{\eta}\,\underline{\eta}^\dagger\underline{P}^\dagger(\lambda')[\Delta\underline{H}-\tfrac{1}{2}\Delta E\underline{S}(\lambda',\lambda)]$$

we have $\quad \mathrm{Tr}\underline{P}(\lambda)\underline{O}_t=0.$ $\qquad (20)$

which is of the same form as the constraints introduced in paper II. In Eq. (20), however, $\underline{O}_t$ is, in general, non-Hermitian whereas our previous constraining operators always satisfied the equation, $\underline{O}\equiv\underline{O}^\dagger$. As we now show the non-Hermitain character of $\underline{O}_t$ presents no particular problem. Thus, consider the $\underline{P}$ equations in a nonorthogonal basis with metric $\underline{S}$,

$$2\underline{P}^3-3\underline{P}^2+\underline{P}-\textstyle\sum_i\mu_i\underline{S}^{-1}\underline{O}_i=\underline{0}, \tag{21}$$

where $-2\mu_i$ is the ith Lagrangian multiplier pertaining to the constraint $2\,\mathrm{Tr}\underline{P}\underline{S}^{-1}\underline{O}_i = O_i$. We now suppose that, in general, $\underline{O}_i \neq \underline{O}_i^\dagger$ and we seek solutions such that $\underline{P} = \underline{R}\underline{S}$ with $\underline{R}$ Hermitian. The hermiticity of $\underline{R}$ is a direct consequence of its factorization as $\underline{C}\underline{C}^\dagger$; the factorization, in turn, is implied by the idempotency of $\underline{P}$. To reiterate, we require that any acceptable solution of Eq. (20) be such that $\underline{P} = \underline{R}\underline{S}$ where $\underline{R} = \underline{R}^\dagger$. It further holds that

$$\underline{P}^\dagger = (\underline{R}\,\underline{S})^\dagger = \underline{S}^\dagger \underline{R}^\dagger = \underline{S}\,\underline{R} = \underline{S}\,\underline{P}\,\underline{S}^{-1} \tag{22}$$

Taking now the Hermitian conjugate of Eq. (21) yields

$$2(\underline{P}^\dagger)^3 - 3(\underline{P}^\dagger)^2 + \underline{P}^\dagger - \sum_i \mu_i \underline{O}_i^\dagger \underline{S}^{-1} = \underline{0} \tag{23}$$

from which, along with Eq. (22), it follows that $\underline{P}$ must also satisfy

$$2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \sum_i \mu_i \underline{S}^{-1} \underline{O}_i^\dagger = \underline{0}. \tag{24}$$

Combining Eqs. (21) and (24) we see that $\underline{P}$ must further satisfy the equation,

$$2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \sum_i \mu_i \underline{S}^{-1} \tfrac{1}{2}[\underline{O}_i + \underline{O}_i^\dagger] = \underline{0}. \tag{25}$$

Of course, all of these equations are equivalent. However, since we use an iterative technique for solving them, only the latter [Eq. (25)] is capable of generating solutions of the desired form, i.e., $\underline{P} = \underline{R}\,\underline{S}$ where $\underline{R} = \underline{R}^\dagger$. In other words, a solution $\underline{P}$ must be such that when multiplied on the right with $\vec{S}$ an Hermitian matrix results.

V. SOME SYMMETRY CONSIDERATIONS

A further result of general relevance is the transformation properties of the $\underline{P}$ equations when symmetry bases are used. In this connection it was shown in paper II that the $\underline{P}$ equations are form invariant under any linear, nonsingular transformation of basis. That is, the usual equation

$$2\underline{P}^3 - 3\underline{P}^2 + \underline{P} - \sum_i \mu_i \underline{S}^{-1} \underline{O}_i = \underline{0} \tag{26}$$

as well as Eq. (25) has the same form in all bases.

Now suppose in addition a particular problem has sufficient symmetry that $\underline{P}$ has a reduced form

$$\underline{P} = \underline{P}_\alpha \oplus \underline{P}_\beta \oplus \cdots \oplus \underline{P}_\nu$$

where $\alpha, \beta, \ldots, \nu$ refer to the irreducible representations of the pertinent symmetry group. In other words, if we know from symmetry considerations that $\underline{P}$ has the preceding form we again may seek solutions of a special type, namely, those that are direct sum constructed. This problem is most elegantly solved by restating it in symmetry-block form. We thus require

$$\underline{P}_\kappa^2 - \underline{P}_\kappa = \underline{0}; \quad \kappa = \alpha, \beta, \ldots, \nu \tag{27}$$

subject to constraints of the form

$$\sum_{\kappa=\alpha}^{\nu} 2\,\mathrm{Tr}\underline{P}_\kappa \underline{S}_\kappa^{-1} \underline{O}_{i\kappa} = O_i; \quad i = 1, 2, \ldots, K \tag{28}$$

where K is the number of constraints necessary to fix the full $\underline{P}$ matrix. We now propose to vary a given block $\underline{P}_\sigma$ holding all others fixed. Since K constraints are sufficient to fully determine $\underline{P}$, we need only K_σ to fully constrain $\underline{P}_\sigma$. Thus our variational problem becomes

$$\delta\,\mathrm{Tr}[\underline{P}_\sigma^2 - \underline{P}_\sigma]^2 = 0 \tag{29}$$

subject to

$$\sum_{\kappa=\alpha}^{\nu} 2\,\mathrm{Tr}\underline{P}_\kappa \underline{S}_\kappa^{-1} \underline{O}_{i\kappa} = O_i,$$

where $i = 1, 2, \ldots, \kappa_\sigma$. In the fully constrained problem, the particular $K_\sigma < K$ constraints is immaterial. If, on the other hand, the problem is not fully constrained, a judicious choice of which constraints to associate with each symmetry block could well be a method for seeking the most acceptable solution of the infinity that must exist when the problem is not fully constrained.

It is clear now that since $\underline{P}_{\kappa \neq \sigma}$ is held fixed in the variation of Eq. (29) it follows that

$$2\underline{P}_\sigma^3 - 3\underline{P}_\sigma^2 + \underline{P}_\sigma - \sum_{i=1}^{K_\sigma} \mu_i \underline{S}_\sigma^{-1} \underline{O}_{i\sigma} = \underline{0}. \tag{30}$$

As usual, the Lagrange multipliers μ_i are determined from the appropriate constraints. They can now be written in the form

$$2\,\mathrm{Tr}\underline{P}_\sigma \underline{S}_\sigma^{-1} \underline{O}_{i\sigma} = O_i - \sum_{\kappa \neq \sigma} 2\,\mathrm{Tr}\underline{P}_\kappa \underline{S}_\kappa^{-1} \underline{O}_{i\kappa}, \tag{31}$$

where the right-hand side is a fixed number.

VI. ΔE AND THE ELECTROSTATIC THEOREM

In Eq. (3) we can obviously let λ and λ' denote coordinates. The resulting ΔE expression can then be cast into a form that relates the one-body density for a given nuclear configuration to the one-body parameter-transition density pertaining to two different configurations. Thus in a polyatomic molecule

$$E(\vec{\mathrm{R}}_\alpha \cdots \vec{\mathrm{R}}_\nu) - E(\vec{\mathrm{R}}_\alpha{}' \cdots \vec{\mathrm{R}}_\nu{}') = \frac{\langle \vec{\mathrm{R}} | \Delta V | \vec{\mathrm{R}}' \rangle}{\langle \vec{\mathrm{R}} | \vec{\mathrm{R}} \rangle}$$

$$= \frac{N \int \Delta V \rho_1(\vec{\mathrm{r}}, \vec{\mathrm{R}}_\alpha \cdots \vec{\mathrm{R}}_\nu, \vec{\mathrm{R}}_\alpha{}' \cdots \vec{\mathrm{R}}_\nu{}')\, d^3r}{\int \rho_1(\vec{\mathrm{r}}, \vec{\mathrm{R}}_\alpha \cdots \vec{\mathrm{R}}_\nu, \vec{\mathrm{R}}_\alpha{}' \cdots \vec{\mathrm{R}}_\nu{}')\, d^3r} \tag{32}$$

which follows from the fact that in a molecular problem the quantity $\Delta\hat{H} = \hat{H}(\vec{\mathrm{R}}) - \hat{H}(\vec{\mathrm{R}}')$ only involves the difference ΔV of one-electron potential energies. Taking the gradient of the left hand side of Eq. (32) with respect to $\vec{\mathrm{R}}_\alpha$ holding $\vec{\mathrm{R}}_\beta \ldots \vec{\mathrm{R}}_\nu$, $\vec{\mathrm{R}}_\alpha{}' \ldots \vec{\mathrm{R}}_\nu{}'$ fixed, we obtain

$$\vec{\nabla}_\alpha E(\vec{\mathrm{R}}_\alpha \cdots \vec{\mathrm{R}}_\nu) = \vec{\nabla}_\alpha \frac{\langle \vec{\mathrm{R}} | \Delta V | \vec{\mathrm{R}}' \rangle}{\langle \vec{\mathrm{R}} | \vec{\mathrm{R}}' \rangle}. \tag{33}$$

Now, using the electrostatic theorem, the left-hand side of this equation becomes the electronic force on the αth nucleus, that is,

$$\int \vec{\nabla}_\alpha(-Z_\alpha/|\vec{\mathrm{r}}-\vec{\mathrm{R}}_\alpha|)\rho_1(\vec{\mathrm{r}},\vec{\mathrm{R}}_\alpha\ldots\vec{\mathrm{R}}_\nu)d^3r$$

$$=\vec{\nabla}_\alpha[\langle\vec{\mathrm{R}}|\Delta V|\vec{\mathrm{R}}'\rangle/\langle\vec{\mathrm{R}}|\vec{\mathrm{R}}'\rangle] \tag{34}$$

which represents an integro-differential relationship between the one-body density of the configuration $\vec{\mathrm{R}}$ and the one-body transition-density between configurations $\vec{\mathrm{R}}$ and $\vec{\mathrm{R}}'$.

This particular form of Parr's ΔE theorem may be viewed as a purely theoretical condition on one-body densities and, therefore, has somewhat the same status as the electrostatic-virial theorem of paper III.[4] Equation (34), however, involves a parameter-transition density whereas the E-V theorem does not. On the other hand, we have shown that in the Hartree-Fock approximation $\rho_1(\vec{\mathrm{r}},\vec{\mathrm{R}},\vec{\mathrm{R}}')$ can be represented in the sense of Eq. (15) in terms of the individual $\vec{\mathrm{R}}$ and $\vec{\mathrm{R}}'$ one-body densities. Thus if for example the $\vec{\mathrm{R}}'$ density is known, then Eq. (34) becomes a purely theoretical constraint on the one-body density for the $\vec{\mathrm{R}}$ configuration.

VII. APPLICATION TO ATOMIC HARTREE-FOCK DENSITIES

In order to test the theorems of Sec. III, we chose to study a simple two-electron atom-ion series. The ground-state electronic wave functions for He, $\mathrm{Li}^+,\ldots,\mathrm{Ne}^{+8}$ have been calculated via Hartree-Fock methods by Clementi.[5] He uses a four- or five-function basis $\underline{\Psi}$ made up of 1*s* functions with different variationally determined scale factors. The single Hartree-Fock atomic function Φ necessary to describe the two electrons is then approximated by $\Phi=\underline{\Psi}\,\underline{C}$, where $\underline{C}$ is the column vector of expansion coefficients.

A. ΔE as a Hartree-Fock Condition

Our first calculation consisted of taking various pairs of Hartree-Fock wave functions for different Z values and using these in Eq. (3). Computationally this imples that we identify the parameter λ with the nuclear charge Z. We then compared

$$\Delta E=\langle Z'|\hat{H}(Z')-\hat{H}(Z)|Z\rangle/\langle Z'|Z\rangle$$

to the actual variational

$$\Delta E=\langle Z'|\hat{H}|Z'\rangle-\langle Z|\hat{H}|Z\rangle.$$

in order to ascertain how well the Hartree-Fock wave functions satisfied Parr's theorem. The results are displayed in Table I. Although not directly connected to the ΔE formalism *per se*, we performed another calculation to corroborate the theorem of paper II relating our method to the Hartree-Fock. The theorem states that the $\underline{P}$ equations will generate true limited Hartree-Fock $\underline{P}$ matrices provided they are fully constrained with Hartree-Fock conditions. Using Clementi's wave functions we computed several expectation values $(T, r^{-2}, r^{-1}, r, r^2r^3)$ which were used as constraints in our iterative $\underline{P}$ equations. With Clementi's four-function basis, three constraints are necessary to completely fix the solution. Thus, for any set of three expectation values used as constraints our equations converged to the Hartree-Fock $\underline{P}$ matrix. The accuracy was limited only by the number of significant figures in Clementi's coefficients.

B. The Expression $R(\lambda',\lambda)$

Our next calculation on the two electron systems was designed to check the expression for the transition density $\underline{R}(\lambda',\lambda)$. This formula, given by Eq. (13), was used again for various pairs of the two electron systems. That is, a transition matrix $\underline{R}(Z',Z)$ was computed using the prescription of Eq. (15). This $\underline{R}(Z',Z)$ matrix was then used to compute ΔE via Eq. (16) which was then compared to our previous, but more directly calculated value of $\Delta E=E(Z')-E(Z)$. $E(Z)$ is the variational value of the energy computed by Clementi. Again, the results in every case agree to the significance of the reported Hartree-Fock $\underline{C}$ matrices. Here the choice of η is immaterial since every column of $\underline{R}(\lambda)$ is obviously proportional to $\underline{C}(\lambda)$ because

$$\underline{R}=\underline{C}\,\underline{C}^\dagger=\begin{pmatrix}C_1\\ \vdots\\ C_n\end{pmatrix}(C_1^*\ldots C_n^*)$$

TABLE I. The comparison of the two independent methods of calculating $\Delta E\equiv E(Z')-E(Z)$ for two-electron Hartree-Fock wave functions.

	$-\Delta E(Z'-Z=1)$ (a.u.)		$-\Delta E(Z'-Z=2)$ (a.u.)		$-\Delta E(Z'-Z=3)$ (a.u.)	
Z	$\langle Z+1\vert\hat{H}\vert Z+1\rangle - \langle Z\vert\hat{H}\vert Z\rangle$	$\langle Z+1\vert\Delta\hat{H}(Z+1,Z)\vert Z\rangle \times\langle Z+1\vert Z\rangle^{-1}$	$\langle Z+2\vert\hat{H}\vert Z+2\rangle - \langle Z\vert\hat{H}\vert Z\rangle$	$\langle Z+2\vert\Delta\hat{H}(Z+2,Z)\vert Z\rangle \times\langle Z+2\vert Z\rangle^{-1}$	$\langle Z+3\vert\hat{H}\vert Z+3\rangle - \langle Z\vert\hat{H}\vert Z\rangle$	$\langle Z+3\vert\Delta\hat{H}(Z+3,Z)\vert Z\rangle \times\langle Z+3\vert Z\rangle^{-1}$
2	4.37473	4.38615	10.74957	10.80771	19.12451	19.26084
3	6.37484	6.38031	14.74978	14.77992	25.12474	25.20219
4	8.37293	8.37815	18.74990	18.76817	31.12488	31.17440
5	10.37496	10.37710	22.74994	22.76231	37.12493	37.15935
6	12.37498	12.37654	26.74997	26.75894	43.12496	43.15036
7	14.37499	14.37621	30.74998	30.75686	49.12497	49.14473
8	16.37499	16.37595	34.74998	34.75545	55.12497	55.14053
9	18.37498	18.37577	38.74998	38.75426	61.12498	61.13757
10	20.37499	20.37558	42.74999	42.75349	67.12499	67.13545

$$= \begin{pmatrix} C_1C_1^* \dots C_1C_n^* \\ C_nC_1^* \dots C_nC_n^* \end{pmatrix}. \quad (35)$$

C. Use of ΔE as a Constraint on the $\underline{P}$ Matrix

Since it is seen from Table I that ΔE is a valid Hartree-Fock condition we are prepared to introduce it as a constraint into our formalism.[6] We first utilized only one ΔE constraint along with any pair of the nontransition constraints listed in Part A. As expected, the solutions of the $\underline{P}$ equations agreed with the Hartree-Fock $\underline{P}$ matrix to an accuracy in correspondence with the reported values. When two ΔE constraints, and one nontransition constraint, were used similar agreement was achieved.

A particularly interesting result was obtained if three ΔE constraints were used. In this case, in addition to the exact agreement with the Hartree-Fock $\underline{P}$, the rate of convergence of the iterative $\underline{P}$ equations was enhanced by three orders of magnitude. More precisely, when we used a given set of three $\underline{P}$ matrices and iterated to the fourth, using only ΔE constraints, less than 10 iterations sufficed to achieve a solution. This is to be compared to 7000 iterations for the one and two ΔE constraint calculations.[7] The remarkable convergence when all ΔE's are used could prove very useful in future calculations.

VIII. DENSITY FITTING IN THE HELIUM ATOM

As already pointed out in the introduction, the $\underline{P}$ equations may also be used in a "density-fitting" context. To clarify this point, suppose that one is given a set of expectation values calculated in a particular basis $\underline{\Psi}$ with density ρ_Ψ. With this information alone one would now like to find ρ_χ as expressed in some other basis $\underline{\chi}$. The least squares method for doing this requires having integrals $\langle\psi_i|\chi_j\rangle$. If this is not convenient, an alternate procedure is possible. Thus, use the available expectation values in the $\underline{\Psi}$ basis (even generating more, if necessary) to constrain the $\underline{P}$ equations. The result will correspond to the representation of the given density in another basis with regions of space weighed according to the choice of expectation values.

This method, although not a least squares, may have at least two advantages. First, it may be numerically inconvenient to compute $\langle\psi_i|\chi_j\rangle$, whereas not so to compute $\langle\psi_i|\hat{O}|\psi_j\rangle$ and $\langle\chi_i|\hat{O}|\chi_j\rangle$ for various operators $\hat{O}$. Second, the type of fit one achieves depends upon the choice of $\hat{O}$. This is an intuitively attractive aspect of the method because one may choose operators $\hat{O}$ that weigh regions of space particularly propitiously with regard to the use one wants to make of the result.

A possible example of this type of calculation might arise in the following way. Suppose one wants to study Hartree-Fock density contours in a region of space close to the nuclei. It would be more convenient to have a large basis SCF density represented in some smaller basis. One, therefore, simply computes SCF expectation values for operators that weigh the region close to the nucleus ($1/r$, for example) and proceeds to generate a $\underline{P}$ matrix for a smaller basis. The resultant density, then, is more convenient to work with and valid in the region desired.

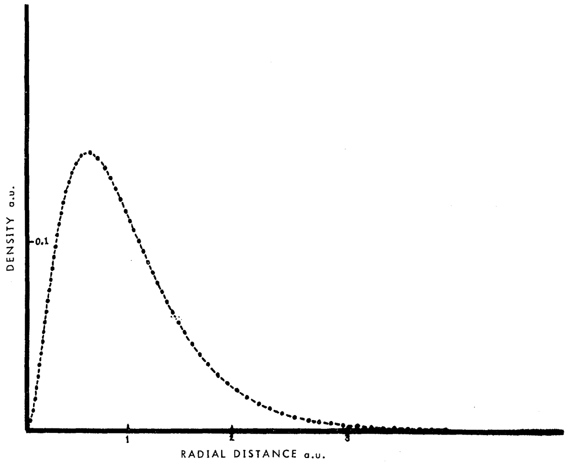

FIG. 1. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and three-function "fit' with $\langle r^{-1}\rangle$ and $\langle r\rangle$ (dashes).

Of course, however, one must be careful not to use the same density well outside its region of validity – as in any fitting procedure.

In Figures 1 through 8, electron density plots are given for various He atom calculations. In these calculations Clementi five-function Hartree-Fock wave functions were used to calculate expectation values of powers of r from $n = -2$ to $n = 8$. These expectation values were then used as constraints in the $\underline{P}$ equations with two- and three-function bases chosen from the Clementi five-function basis. In all the figures, both Hartree-Fock and the smaller basis, "fits" are plotted.

We note several things about these density plots. First of all, in several cases (Figs. 1–4), we can

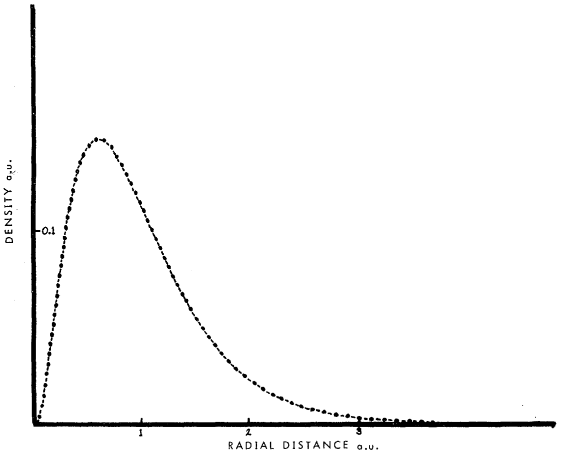

FIG. 2. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and three-function "fit" with $\langle r\rangle$ and $\langle r^2\rangle$ (dashes).

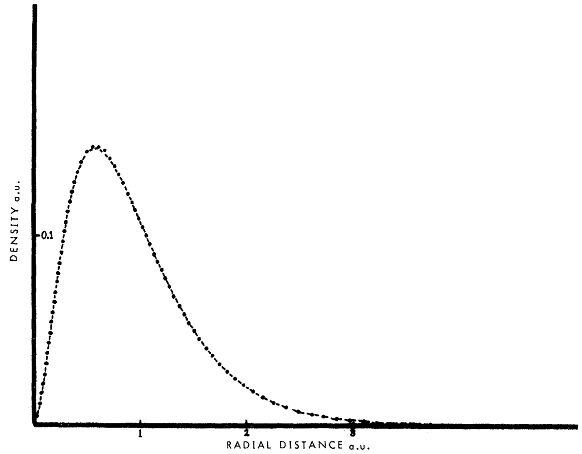

FIG. 3. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and two-function "fit" with $\langle r\rangle$ (dashes).

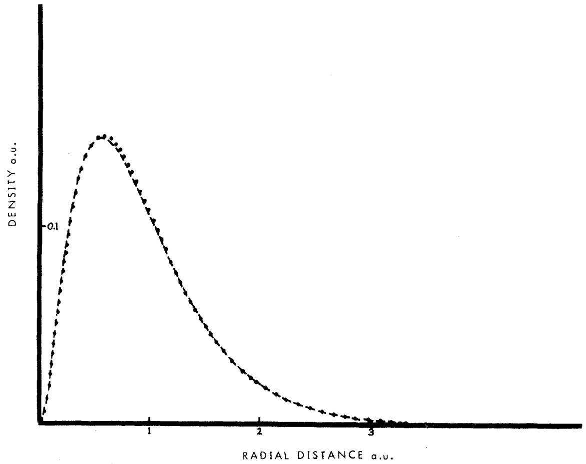

FIG. 5. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and three-function "fit" with $\langle r^3\rangle$ and $\langle r^4\rangle$ (dashes).

detect little or no difference between the five-function Hartree-Fock and the two- and three-function fits. These results occur if the powers of r are such that the region of space singled out is the region of maximum density – this can be done either with sets involving r^{-1}, r, and r^2 or (less well) average sets such as r^{-2} and r^{+8}, etc. Our first conclusion, then, is that He atom Hartree-Fock can be fit (with accuracy of ~0.01%) to considerably smaller, more tractable bases, if the expectation value constraints are suitably chosen. If this result obtains, in larger systems, it could be well worthwhile for generating bases for bigger calculations. Secondly, we note that as the powers of r increase (Figs. 5 and 6 for example), the "out-far" region is fit well at the expense of the "in-close" region. This is a result to be expected, showing that some intuition can be used in choosing constraints. A word of caution is in order here, however, since it is clear that the choice of operators used to fit the density is correlated with the choice of basis, both must be chosen in some reasonable way. Our previous atomic calculations indicate that any set of operators that single out the space natural to the atomic system ($r \sim 1$ a.u. in He) will work well in conjunction with an approximately variational basis. On the other hand, even the scale factors of the basis can be adjusted by putting more constraints on the problem and varying the scale factors until a solution is reached. In this way, a "best" fit to a limited size basis, with a given set of operators, can be achieved.

This investigation of the use of the $\underline{P}$ equations in a density fitting role is only preliminary. To complete it, we should do a comparison study with a least-squares method. We, nonetheless, reiterate some of the possible advantages of the present method. In the first place, a least-squares method requires overlap integrals between one basis and another. In general, this could cause some nu-

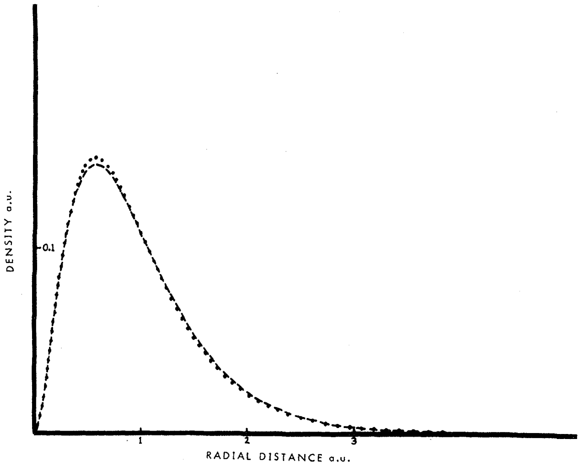

FIG. 4. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and three-function "fit" with $\langle r^{-2}\rangle$ and $\langle r^8\rangle$ (dashes).

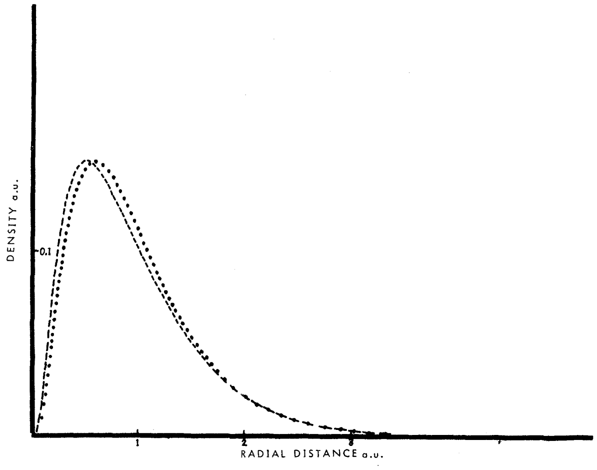

FIG. 6. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and three-function "fit" with $\langle r^5\rangle$ and $\langle r^6\rangle$ (dashes).

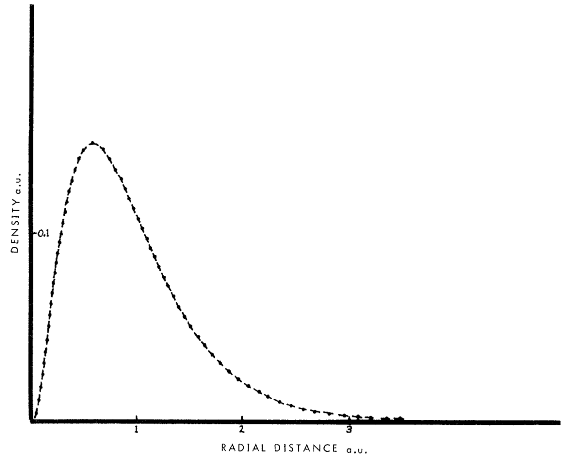

FIG. 7. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and two-function "fit" with $\langle r^3\rangle$ (dashes).

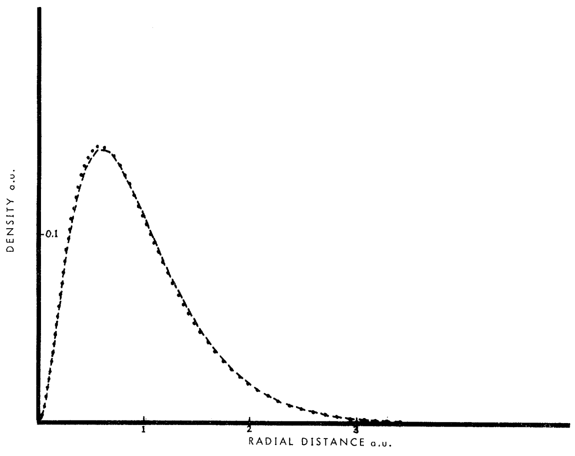

FIG. 8. Comparison of $r^2\rho$ versus r for five-function Hartree-Fock (dots) and two-function "fit" with $\langle r^6\rangle$ (dashes).

merical difficulties if the bases are not compatible in the sense of leading to integrals that can be done analytically. Our method requires no such "transition" integrals. Secondly, least-squares methods are not unique in that an arbitrary weighing factor $\omega(\vec{r})$ can (and should) always be inserted into the least-squares condition,

$$\delta\int|\Phi(\vec{r})-\sum_i c_i\Psi_i(\vec{r})|^2\omega(\vec{r})d^3r=0\ .$$

This free choice of weighting factor, of course, plays the role of our free choice of constraining operators. In the final analysis, then, it becomes a matter of what one has more easily available and which method best suits one's needs. Our main purpose here is to describe this new independent way of fitting densities to smaller bases.

IX. CONCLUSION

Our main purpose in this paper has been twofold. First, we investigated the use of Parr's finite difference ΔE theorem as a constraint on our idempotency equation. All the necessary formalism was developed and tested in several applications in small atoms. It appears that the role of the ΔE theorem in this method will be not unlike the electrostatic-virial equation of paper III. Thus, as a density continuation formula, this constraint shows much promise. It can be used in both a semi-empirical and a theoretical context. The second aspect of this work is found in the suggestion and application of the use of the P equation to represent (or fit) Hartree-Fock densities in smaller, more tractable bases.

It was shown that the property of the P equations to select any pure state, given its expectation values, can be used to advantage in this regard. Thus although not a least-squares method, the approach affords what may be called a more "local" fit in the sense that expectation values may be chosen to single out a given region of space where the density perhaps is more important. What this "fit" corresponds to is a projection of the Hartree-Fock state onto a subspace of the original Hartree-Fock Hilbert space. Thus depending upon one's interest in the Hartree-Fock in the first place, this subspace may be chosen for either tractability or physical attractiveness, or both (e.g., the representation of a molecular Hartree-Fock function in a simple Slater type basis, choosing expectation value constraints that emphasize the quantities of interest).

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*This work was supported by the Advanced Research Projects Agency under Army Contract No. DA-31-124-ARO(D)-14.

[1] W. L. Clinton, A. J. Galli, and L. J. Massa, Phys. Rev. 177, 7 (1969); paper II of this series.

[2] R. Parr, J. Chem. Phys. 40, 3726 (1964). A simple proof goes as follows: Given two Hamiltonian operators $\hat{\mathcal{H}}(\lambda)$, $\hat{\mathcal{H}}(\lambda')$ for an N-body system, diagonal in their respective bases $|\lambda\rangle$ and $|\lambda'\rangle$. Here λ' and λ are two arbitrary parameters. Then $\hat{\mathcal{H}}(\lambda')|\lambda'\rangle=E(\lambda')|\lambda'\rangle$ and $\hat{\mathcal{H}}(\lambda)|\lambda\rangle=E(\lambda)|\lambda\rangle$ which upon multiplying the first by $\langle\lambda|$ and the second by $\langle\lambda'|$ yields after subtraction

$$E(\lambda')-E(\lambda)=\langle\lambda'|\hat{\mathcal{H}}(\lambda')-\hat{\mathcal{H}}(\lambda)|\lambda\rangle/\langle\lambda'|\lambda\rangle\ .$$

In the last step the Hermitian property of $\hat{\mathcal{H}}$ has been used. If $\hat{\mathcal{H}}(\lambda)$ can be written in the form

$$\hat{\mathcal{H}}(\lambda)=\sum_i^N\hat{H}_i(\lambda)+\sum_{i>j}^N\hat{H}_{ij}\ ,$$

i.e., only the one-body term depends upon the parameters λ, then

$$\hat{\mathcal{H}}(\lambda')-\mathcal{H}(\lambda)=\sum_i^N[\hat{H}_i(\lambda')-\hat{H}_i(\lambda)]\ .$$

Parr's theorem now follows in the form

$$\Delta E=\sum_i \langle\lambda'|\hat{H}_i(\lambda')-\hat{H}_i(\lambda)|\lambda\rangle/\langle\lambda'|\lambda\rangle$$

$$=N\langle\lambda'|H(\lambda')-H(\lambda)|\lambda\rangle/\langle\lambda'|\lambda\rangle\ ,$$

where H is any one of the one-body terms. Equation (3) now follows upon substitution of the spinless transition density explicitly defined as

$$\rho_1(\vec{r}_1{}',\vec{r}_1,\lambda',\lambda)$$

$$\equiv N\sum_{s_1\cdots s_n}\int\Psi^*(\vec{r}_1{}'s_1{}'\cdots\vec{r}_n{}'s_n{}'\lambda')$$

$$\times\Psi(\vec{r}_1 s_1\cdots\vec{r}_n s_n,\lambda)d^3r_2\cdots d^3r_n\ .$$

In the text for $\rho_1(\vec{r}_1{}',\vec{r}_1,\lambda\cdot,\lambda)$ (the transition density), we use the shorthand notation $\rho_1(\lambda',\lambda)$.

[3] A specific example involving η is given in Sec. VII B.

[4] W. L. Clinton, G. A. Henderson, and J. V. Prestia, Phys. Rev. 177, 13 (1969); paper III of this series, preceding paper.

[5] E. Clementi, J. Chem. Phys. 38, 996 (1963).

[6] It should be noted [viz. Eqs. (19) and (20)] that the use of K transition constraints requires one to know K of the $\underline{P}$ matrices in order to iteratively generate the unknown $(K+1)$th $\underline{P}$ matrix.

[7] The rate of convergence of Eq. (26) depends on the initial guess and on the choice of constraints. The number of iterations necessary to achieve idempotency $[\mathrm{Tr}(\underline{P}^2-\underline{P})^2\sim10^{-8}]$ varies markedly; the 7000 is our worst case. See paper V for a more thorough discussion of optimum convergence.

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Direct Determination of Pure-State Density Matrices. V. Constrained Eigenvalue Problems[*]

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A density-matrix approach to constrained eigenvalue problems is presented. It is shown that all of the linearly independent eigenvectors of an Hermitian matrix can be generated with the idempotency equations ($\underline{P}$ equations) developed in previous papers of this series. In particular, the method is applied to variational calculations in $H_2{}^+$ and He.

Since the local-energy method assumes eigenvalue form, it also can be formulated in terms of the $\underline{P}$ equations. Various local energies for $H_2{}^+$ and He are calculated. Direct methods of incorporating local energies as constraints are suggested. An orthogonal operator formalism for the $\underline{P}$ equations is given. Such operators $\underline{O}_k,\underline{O}_l$ have the property that $\mathrm{Tr}\underline{O}_k\underline{O}_l=0$ for $k\neq l$. The iterative $\underline{P}$ equations, then, assume the simple form

$$\underline{P}_{n+1}=\mathcal{P}_n+\sum_k[(O_k-\mathrm{Tr}\mathcal{P}\underline{O}_k)/\mathrm{Tr}\underline{O}_k{}^2]\underline{O}_k\ ,$$

where $\mathcal{P}\equiv3\underline{P}^2-2\underline{P}^2$ and the constraints, $\mathrm{Tr}\underline{P}\,\underline{O}_k=O_k$, are now identically satisfied.

I. INTRODUCTION

In papers I–IV of this series,[1] a method was developed for the calculation of one-body density matrices. In the present paper it will be shown that the method is also applicable to general eigenvalue theory. In particular, it will be seen that the constrained $\underline{P}$ equations of paper II can be used to generate all of the linearly independent eigenvectors of an Hermitian matrix by casting the eigenvalue equation into constraint form. The present approach allows other theoretical or empirical constraints to be included into the eigenvalue problem; thus it is particularly suited for constrained energy-variational calculations.[2] The method is applied to both eigenvalue and pseudo-eigenvalue (non-unit metric) problems with and without additional "non-eigenvalue" constraints.

The present paper deals with eigenvalue theory in a nonconventional way. Thus an enumeration of the applications of the $\underline{P}$ equations investigated to date will be given in order to establish a context in which the current work is to be viewed.

1. *Semiempirical Constraints.* It was shown in papers I and II that the electrostatic and virial theorems can be used to generate reasonable first-order density kernels using experimental data. These densities can be made quantum-mechanically valid by using the $\underline{P}$ equations. The use of hypervirial[3] constraints was also suggested as an area of future investigation. Clearly, any observable (e.g., empirical) moments of a charge distribu-