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-

tion can also be employed as a constraint.

2. *Theoretical Constraints.* In paper III, a purely theoretical constraint (the electrostatic-virial theorem) was shown to be effective in generating reasonable densities. In the present paper, we investigate further theoretical constraints.

3. *Mixed Constraints.* It is obvious that any combination of 1. and 2. is possible. We will see, for example, that in the energy eigenvalue problem the number of Hamiltonian matrix elements that need be calculated is reduced in proportion to the number of available empirical conditions. This is a consequence of the particular form of the eigenvalue constraints.

4. *Fitting Densities to Other Bases.* In paper IV it was seen that Hartree-Fock (HF) densities in one basis set can be "operator fitted" to another basis set, provided sufficient expectation values are available. It was pointed out there that the method may offer some advantages over the usual least-squares technique.

5. *Continuation of Hartree-Fock Densities.* In paper III, an expression for the derivative of an idempotent density matrix was derived. The derivative matrix $d\underline{P}/d\lambda$ allows one to obtain $\underline{P}(\lambda+\Delta\lambda)$ if $\underline{P}(\lambda)$ is known. In general, λ is any parameter of the system (e.g., R, Z, m, etc.).

6. *Eigenvalue Theory.* The theoretical and practical aspects of eigenvalue theory form the subject matter of the present paper.

Finally, a remark concerning the scope of the $\underline{P}$ equations is in order. In general, all idempotent density matrices are solutions of these equations. In particular, two classes of considerable interest are: (a) reduced Hartree-Fock density matrices, e.g., the one- and two-body density matrices $\rho_1(1',1)$ and

$$\rho_2(1'2',12)=\tfrac{1}{2}[\rho_1(1',1)\rho_2(2',2)-\rho_1(1',2)\rho_2(2',1)];$$

(b) any density matrix of the form

$$\rho(x',x)=\Psi^*(x')\Psi(x),$$

where x represents any set of coordinates. The eigenvalue theory of the following sections is concerned mainly with this broader class (b).

II. A DENSITY-MATRIX APPROACH TO EIGENVALUE PROBLEMS

A. Discrete Representations

We begin by casting the eigenvalue problem for an Hermitian matrix into density-matrix form. Consider

$$\underline{A}\,\underline{C}_i=\epsilon_i\underline{C}_i;\quad \underline{C}_i^{\dagger}\underline{C}_j=\delta_{ij};\quad \underline{A}=\underline{A}^{\dagger} \tag{1}$$

which imply a set of density matrix equations, once we define $\underline{P}_i\equiv\underline{C}_i\underline{C}_i^{\dagger}$. Thus

$$\underline{A}\,\underline{P}_i=\epsilon_i\underline{P}_i;\quad \underline{P}_i\underline{P}_j=\underline{P}_j\delta_{ij};\quad \underline{P}_i=\underline{P}_i^{\dagger}, \tag{2}$$

and one also easily sees that

$$[\underline{A},\underline{P}_i]=\underline{0};\quad \mathrm{Tr}\underline{P}_i\underline{A}=\epsilon_i;\quad \mathrm{Tr}\underline{P}_i=1. \tag{3}$$

Furthermore, it has been shown that[4] $\underline{P}_i^2=\underline{P}_i$ and $\mathrm{Tr}\underline{P}_i=1$ constitute necessary and sufficient conditions for factorization in the form $\underline{P}_i=\underline{C}_i\underline{C}_i^{\dagger}$. It was also shown in paper II that a finite number κ of constraints will determine any m-dimensional Hermitian, idempotent matrix $\underline{P}$.[1] Such a matrix can be generated with the iterative equation

$$\underline{P}_{n+1}=3\underline{P}_n^{\,2}-2\underline{P}_n^{\,3}+\sum_{k=1}^{\kappa}\lambda_k\underline{O}_k \tag{4}$$

obtained from $\delta\mathrm{Tr}(\underline{P}^2-\underline{P})^2=0$ subject to constraints of the form $\mathrm{Tr}\underline{P}\underline{O}_k=O_k$ with Lagrange multipliers $-2\lambda_k$. We therefore need only to convert Eqs. (2) and (3) to constraint form; this can be done as follows. Define an m-square matrix $\underline{O}(kl)$ such that $(\underline{O}(kl))_{k'l'}=\delta_{kk'}\delta_{ll'}$. One then easily sees that

$$\mathrm{Tr}\underline{O}(kl)[\underline{A}-\epsilon_i\underline{1}]\underline{P}_i=\{[\underline{A}-\epsilon_i\underline{1}]\underline{P}_i\}_{lk}, \tag{5a}$$

$$\mathrm{Tr}\underline{O}(kl)[\underline{A},\underline{P}_i]=[\underline{A},\underline{P}_i]_{lk}, \tag{5b}$$

so that every matrix element of the eigenvalue Eqs. (2) and (3) can be generated via Eqs. (5). These can be rewritten as

$$\mathrm{Tr}\underline{P}_i\underline{O}(kl)[\underline{A}-\epsilon_i\underline{1}]=0, \tag{6a}$$

$$\mathrm{Tr}\underline{P}_i[\underline{O}(kl),\underline{A}]=0. \tag{6b}$$

Equations (6) constitute two alternative (but not independent) sets of eigenvalue constraints to be used in Eq. (4). Equation (6b) offers the better set of constraints from a computational standpoint, since the constraining matrix $[\underline{O}(kl),\underline{A}]$ does not depend upon $\underline{P}_i$ unless $\underline{A}$ does. By contrast, Eq. (6a) has an additional $\underline{P}$ dependence via $\epsilon_i=\mathrm{Tr}\underline{P}_i\underline{A}$ so that the constraining matrix $(\underline{A}-\epsilon_i\underline{1})$ must be recomputed at every iteration.

It is clear that completely arbitrary matrices can be used in place of $\underline{O}(kl)$, since, for example, $\mathrm{Tr}\underline{O}[\underline{P}_i,\underline{A}]=0$ at solution for every $\underline{O}$. We will discuss later some attempts to choose $\underline{O}$ so as to optimize convergence. On the other hand, in the event $\underline{A}$ corresponds to a Hamiltonian matrix $\underline{H}$, the $\underline{O}(kl)$ constraints allow one to avoid the calculation of some of the matrix elements $(\underline{H})_{ij}$ since only the kth column and lth row of $\underline{H}$ are necessary per $\underline{O}(kl)$ constraint. These constraints then can be augmented with empirical or other theoretical conditions.

In using Eq. (6a) as a set of constraints, we note that the eigenvalue must be stationary at solution. Consequently, the handling of these constraints is particularly simple. Thus we can write

$$\mathrm{Tr}\delta\underline{P}_i\underline{O}(kl)[\underline{A}-\epsilon_i\underline{1}]=0, \tag{7}$$

because $\delta\epsilon_i=0$ at solution. Therefore Eq. (7) may be treated as an ordinary constraint, except that $\epsilon_i^{(n)}\equiv\mathrm{Tr}(\underline{P}_i)_n\underline{A}$ must be computed at each iteration. It will now be shown that all of the linearly independent eigenvectors of the matrix $\underline{A}$ can be generated by incorporating the orthogonality conditions

$\underline{P}_i\underline{P}_j = \underline{0}$ as constraints into our formalism. The total solution of the eigenvalue problem then takes the following form. In the usual way, we seek a solution $\underline{P}_i$ that satisfies

$$\underline{P}_i^2 = \underline{P}_i ; \quad \mathrm{Tr}\underline{P}_i = 1;$$

$$\mathrm{Tr}\underline{P}_i\{[\underline{O}(k,l),\underline{A}] + [\underline{O}(k,l),\underline{A}]^\dagger\} = 0 . \qquad (8)$$

In this case, Eq. (4) becomes

$$(\underline{\mathcal{P}}_i)_{n+1} = (\underline{\mathcal{P}}_i)_n + \lambda_1{}^{(n)}\underline{1} + \sum_{k\neq l}^{K} \lambda_{kl}{}^{(n)}$$

$$\times \{[\underline{O}(k,l),\underline{A}] + [\underline{O}(kl),\underline{A}]^\dagger\} , \qquad (9)$$

where $(\underline{\mathcal{P}}_i)_n \equiv 3(\underline{P}_i{}^2)_n - 2(\underline{P}_i{}^3)_n$. Having generated the first $\underline{P}_i$ (and, therefore, a $\underline{C}_i$) we now require

$$\underline{P}_j^2 = \underline{P}_j ; \quad \mathrm{Tr}\underline{P}_j = 1; \quad \mathrm{Tr}\underline{P}_j\underline{P}_i = 0 ,$$

$$\mathrm{Tr}\underline{P}_j\{[\underline{O}(kl),\underline{A}] + [\underline{O}(kl),\underline{A}]^\dagger\} = 0 . \qquad (10)$$

The solution $\underline{P}_j$ must then correspond to another linearly independent eigenvector $\underline{C}_j$. The reason for this is that if solutions of Eqs. (8) and (10) exist, then $\underline{P}_i = \underline{C}_i\underline{C}_i{}^\dagger$ and $\underline{P}_j = \underline{C}_j\underline{C}_j{}^\dagger$ so that

$$\mathrm{Tr}\underline{P}_i\underline{P}_j = \mathrm{Tr}\underline{C}_i\underline{C}_i{}^\dagger\underline{C}_j\underline{C}_j{}^\dagger = |(\underline{C}_i{}^\dagger\underline{C}_j)|^2$$

is zero if and only if $\underline{C}_i$ and $\underline{C}_j$ are linearly independent. Indeed, the nontrivial solutions of Eqs. (8) and (10) must be orthogonal so that even degenerate eigenvectors are automatically orthogonalized by this method. One now simply continues in this fashion until all of the m linearly independent eigenvectors are generated.[6] This formalism has been verified in several sample calculations.

We next consider $\underline{A}\underline{C}_i = \epsilon_i\underline{S}\underline{C}_i$, which is often referred to as a pseudo-eigenvalue equation. This can be immediately converted to an ordinary eigenvalue problem if $\underline{S}$ is nonsingular. Thus define $\bar{\underline{A}} \equiv \underline{S}^{-1}\underline{A}$, so that

$$\bar{\underline{A}}\underline{C}_i = \epsilon_i\underline{C}_i ; \quad \bar{\underline{A}}^\dagger \neq \bar{\underline{A}} . \qquad (11)$$

Defining, in addition, $\underline{P}_i \equiv \underline{C}_i\underline{C}_i{}^\dagger\underline{S}$ and requiring $\underline{C}_i{}^\dagger\underline{S}\underline{C}_i = 1$, one again obtains $\underline{P}_i{}^2 = \underline{P}_i$. The constraints can now be formulated much as before except that the first of Eqs. (3) becomes by virtue of Eq. (11) a pseudocommutation relation

$$\bar{\underline{A}}\underline{P}_i\underline{S}^{-1} - \underline{P}_i\underline{S}^{-1}\bar{\underline{A}}^\dagger = \underline{O} . \qquad (12)$$

As a check on this pseudo-eigenvalue formalism, Eq. (12) was used in constraint form to reproduce the variational results of James[7] for the ground electronic state of the $H_2{}^+$ molecule. The James basis set consisted of the two functions, $\exp(-\alpha\xi)$ and $\eta^2\exp(-\alpha\xi)$ with $\alpha = 1.35$. We also have performed $H_2{}^+$ calculations, using three- and four-function bases chosen out of the general set

$$\{\xi^n\eta^m e^{-\alpha\xi}\} .$$

We next consider the eigenvalue problem in which $\underline{A}$ depends upon its own eigenvectors. In the Hartree-Fock problem, for example, $\underline{A} = \underline{A}(\underline{P})$.[8] This form of $\underline{A}$ requires a slightly modified approach in deriving the $\underline{P}$ equations, since now variations in $\underline{P}$ imply also variations in $\underline{A}$. Proceeding as before, we obtain constraints of the form

$$\mathrm{Tr}\underline{P}[\underline{O},\underline{A}] = 0 \quad . \qquad (13)$$

A variation $\delta\underline{P}$ now implies

$$\mathrm{Tr}\,\delta\underline{P}[\underline{O}(kl),\underline{A}] + \mathrm{Tr}\underline{P}[\underline{O}(kl),\delta\underline{A}] = 0 . \qquad (14)$$

But $\delta\underline{A} \equiv \underline{A}(\underline{P} + \delta\underline{P}) - \underline{A}(\underline{P})$, or

$$\delta(\underline{A})_{\alpha\beta} = \sum_{\alpha',\beta'} \frac{\partial(A)\alpha\beta}{\partial(\underline{P})_{\alpha'\beta'}}\,\delta(\underline{P})_{\alpha'\beta'}$$

$$\equiv \mathrm{Tr}(\underline{A}')_{\alpha\beta}\,\delta\underline{P} ,$$

where the matrix $(\underline{A}')_{\alpha\beta}$ has elements

$$\frac{\partial(\underline{A})_{\alpha\beta}}{\partial(\underline{P})_{\alpha'\beta'}} .$$

Equation (14) becomes now

$$\mathrm{Tr}\,\delta\underline{P}_i\{[\underline{O}(kl),\underline{A}]$$

$$+ \sum_{\alpha,\beta,\gamma} (\underline{P}_i)_{\beta\gamma}(\underline{O}(kl))_{\gamma\alpha}(\underline{A}')_{\alpha\beta}$$

$$- \sum_{\alpha,\beta,\gamma} (\underline{P}_i)_{\beta\gamma}(\underline{A}')_{\gamma\alpha}(\underline{O}(kl))_{\alpha\beta}\} = 0 , \qquad (15)$$

or since $(\underline{O}(kl))_{\gamma\alpha} = \delta_{k\gamma}\delta_{l\alpha}$

$$\mathrm{Tr}\,\delta\underline{P}_i\{[\underline{O}(kl),\underline{A}] + \textstyle\sum_\beta (\underline{P}_i)_{\beta k}(\underline{A}')_{l\beta}$$

$$- \sum_\gamma (\underline{P}_i)_{l\gamma}(\underline{A}')_{\gamma k}\} = 0 . \qquad (16)$$

In the Hartree-Fock case, $\underline{A}$ is the Fock Hamiltonian matrix $\underline{F}$ and depends on $\underline{P}$ through the self-consistent-field (SCF) potential term which is linear in the elements of $\underline{P}$. In this case $(\underline{A}')_{\alpha\beta}$ is simple to calculate.

The method has been used to solve the He-atom Hartree-Fock equation. In these calculations Clementi bases[10] were used.

Another type of eigenvalue problem of relevance in quantum mechanics derives from the energy-variance minimization procedure. Thus, defining the variance $V \equiv \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2$, we have

$$\delta\{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2\} = 0; \quad \langle \hat{1} \rangle = 1 , \qquad (17)$$

where $\hat{H}$ is the Hamiltonian of the system and, in general, $\langle \hat{O} \rangle \equiv \int \Psi^* \hat{O} \Psi dq$. Alternatively, $\langle \hat{O} \rangle$ can be defined via a discrete sum average as in the local energy method.[11] Equations (17) imply the eigenvalue equation

$$\{\hat{H}^2 - 2\langle \hat{H} \rangle \hat{H} - \lambda\}\,\Psi = 0 , \qquad (18)$$

where the Lagrangian multiplier is given by λ

$=\langle \hat{H}^2\rangle - 2\langle \hat{H}\rangle^2$. Since Eq. (18) is an eigenvalue equation, the preceding density-matrix formalism is immediately applicable.

B. Mixed Representations

Consider now the eigenvalue equation

$$\hat{A}(x)\Psi(x) = \epsilon_i \Psi(x);\qquad \int dx\, \Psi_i^*(x)\Psi_j(x) = \delta_{ij}\,, \tag{19}$$

where x represents a set of coordinates and $\hat{A}(x)$ is an Hermitian operator. Defining the density matrix in the x representation as

$$\rho_i(x', x) \equiv \Psi_i^*(x')\Psi_i(x)\,,$$

Eq. (19) becomes

$$A(x)\rho_i(x', x) = \epsilon_i \rho_i(x', x)\,. \tag{20}$$

Introducing, in addition, the discrete basis $\underline{\chi}$ via $\Psi_i = \underline{\chi}\,\underline{C}$ and defining as usual $\underline{P_i} \equiv \underline{C_i}\,\underline{C_i}^\dagger$, $\rho_i(x', x)$ becomes

$$\rho_i(x', x) = \mathrm{Tr}\underline{P}_i\, \underline{\chi}^\dagger(x')\underline{\chi}(x)\,. \tag{21}$$

Inserting Eq. (21) into Eq. (20), we obtain

$$\mathrm{Tr}\underline{P}_i\, \underline{\chi}^\dagger(x')\hat{A}(x)\underline{\chi}(k) = \epsilon_i\, \mathrm{Tr}\underline{P}_i\, \underline{\chi}^\dagger(x')\underline{\chi}(x); \tag{22}$$

or, defining

$$\underline{A}(x', x) \equiv \underline{\chi}^\dagger(x')\hat{A}(x)\underline{\chi}(x)$$

and $\underline{S}(x', x) \equiv \underline{\chi}^\dagger(x')\underline{\chi}(x)$,

we see that

$$\mathrm{Tr}\underline{P}_i\,[\underline{A}(x', x) - \epsilon_i \underline{S}(x', x)] = 0\,. \tag{23}$$

This is a mixed representation analog of Eq. (5a). In principle, Eqs. (23) can be used as constraints to completely determine the eigenfunction $\Psi_i(x)$ in the χ basis set. However, in a truncated basis set different results will be obtained, depending upon the set of points (x', x) at which the constraints are applied.

A measure of the adequacy of the basis set in representing the eigenfunction is the constancy of the "local eigenvalue"

$$\epsilon(x) \equiv \hat{A}(x)\Psi(x)/\Psi(x)\,. \tag{24}$$

This quantity has been calculated and is plotted in Figs. 1–4, for H_2^+ and He. In H_2^+

$$\hat{A}(x) \equiv -\tfrac{1}{2}\nabla^2 - 1/r_A - 1/r_B\,,$$

and in He

$$\hat{A}(x) \equiv -\tfrac{1}{2}\nabla^2 - Z/r + \int d^3r'\, |\Psi(\vec{r}\,')|^2/|\vec{r} - \vec{r}\,'|\,.$$

James's function[7] $\Psi(\xi, \eta) \sim (1 + a\eta^2)\exp(-2\xi)$ was used for H_2^+ (Fig. 1). For He, a best atom (Fig. 2) and two different Hartree-Fock functions[10] (Figs. 3 and 4) were used. The fact that these local energies are reasonably constant over a significant range of the variables, even though the basis sets are small, suggests that the ambiguity regarding the choice of points need not be a serious limitation. That is, any choice of points in the region of constancy will generate essentially the same density matrix. The poor large-r behavior of the He-atom local energies (Figs. 3 and 4) could be avoided by requiring that $\epsilon(\infty)$ be equal to the χ basis set Hartree-Fock eigenvalue [i.e., $\epsilon(\infty) = \overline{\epsilon}_{\mathrm{HF}} \equiv \mathrm{Tr}\underline{PF}$, where $\underline{F}$ is the Fock operator in the χ basis]. In the present case $\chi_i \sim \exp(-\alpha_i r)$, implying the condition $\epsilon(\infty) = \mathrm{Tr}\underline{PF} = -\alpha_1^2/2$, where α_1 is the smallest exponent in the χ basis set. Clementi's calculation includes a base function with $\alpha = 0.59$, thereby leading to a poor local energy as $r \to \infty$.

Other special constraints derive from the singularities in the potential when viewed in the x representation. In particular, in atomic and molecular theory the singularities are of the Coulomb type and the concomitant conditions on the wave function are called cusp conditions.[12] As Bingle[13] has shown, these cusp conditions can be put in density-matrix form. Corresponding to the nuclear attraction term $-\sum_{\alpha,i} Z_\alpha/r_{i\alpha}$, where $r_{i\alpha}$ is the distance be-

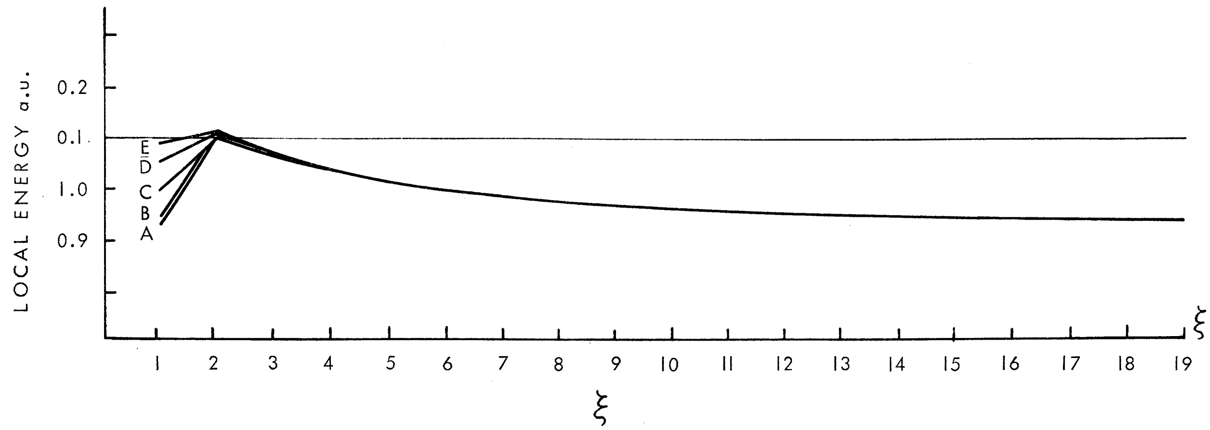

FIG. 1. Local energies for the James functions in H_2^+. The abscissa is the spheroidal variable ξ. The curves A through E correspond to $\eta = 0.2$, 0.4, 0.6, and 0.8.

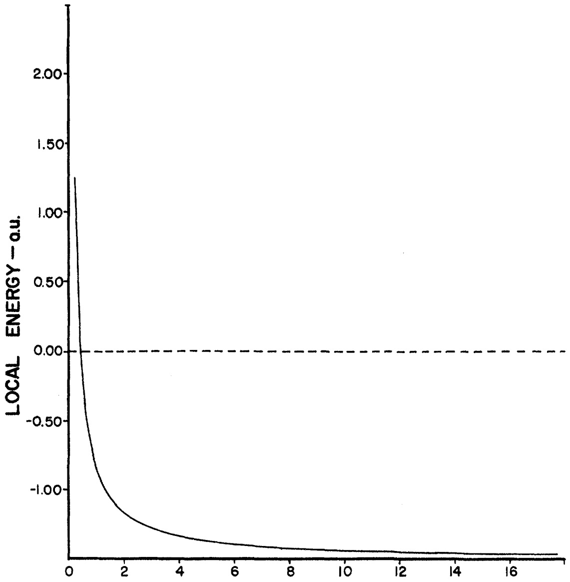

FIG. 2. Local SCF eigenvalue versus r for the helium best-atom function $\Phi = (\zeta^{3/2}/\pi^{1/2})\ \exp(-\zeta r)$; $\zeta = 1.6875$.

tween the ith electron and αth nucleus of charge Z, one has the cusp condition

$$\left.\frac{\partial\Psi(\vec{r}_1\vec{r}_2\cdots\vec{r}_n)}{\partial r_{i\alpha}}\right|_{r_{i\alpha}=0} = -Z_\alpha\Psi(\vec{r}_1\vec{r}_2\cdots\vec{r}_n)\Big|_{r_{i\alpha}=0}, \tag{25}$$

and here the infinite nuclear-mass approximation has been invoked. Multiplying Eq. (25) by

$$\Psi^*(\vec{r}_1\vec{r}_2\cdots\vec{r}_n)\,|_{r_{i\alpha}=0}\ ,$$

summing over i, and integrating over all electronic coordinates except the ith, it follows that

$$\left.\frac{\partial\rho_1(\vec{r}\,',\vec{r},\vec{R}_\alpha\cdots\vec{R}_\nu)}{\partial|\vec{r}-\vec{R}_\alpha|}\right|_{\substack{|\vec{r}-\vec{R}_\alpha|=0\\ \vec{r}\,'=\vec{r}}}$$

$$= -Z_\alpha\rho_1(\vec{r},\vec{R}_\alpha\cdots\vec{R}_\nu)\Big|_{|\vec{r}-\vec{R}_\alpha|=0}. \tag{26}$$

In this form, the cusp condition can be used as a constraint in the $\underline{P}$ equations.

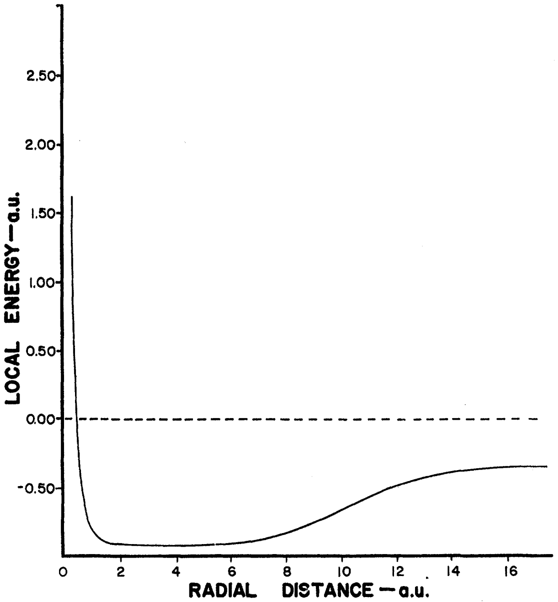

FIG. 3. Local SCF eigenvalue versus r for the helium Clementi 5-function basis.

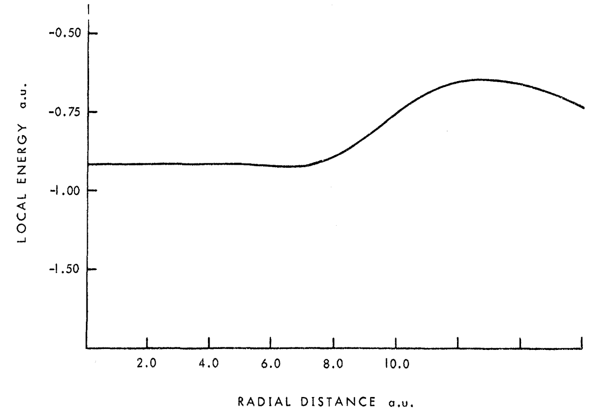

FIG. 4. Local SCF eigenvalue versus r for the Roothaan-Sachs-Weiss 12-function exponential-polynomial basis.

Thus far we have considered the applications of the $\underline{P}$ equations to several important types of eigenvalue problems. The main value of the present method would appear to be not so much that it represents an alternative eigenvalue technique, but rather the ease with which additional constraints can be incorporated.

III. FORMULATION OF THE $\underline{P}$ EQUATIONS IN ORTHOGONAL OPERATORS

In all of our previous work we have had to determine the Lagrangian multipliers λ_k of Eq. (4) by solving a set of linear inhomogeneous equations of the form

$$\underline{\tau}\underline{\lambda}^{(n)} = \underline{\Delta}^{(n)}; \tag{27}$$

where $(\underline{\tau})_{kl} \equiv \mathrm{Tr}\underline{O}_k\underline{O}_l$ and

$$(\underline{\Delta}^{(n)})_k \equiv (O_k - \mathrm{Tr}\underline{\mathcal{P}}_n\underline{O}_k).$$

This must be done at every iteration.

We now show that this phase of the calculation can be reformulated to considerable advantage. The formulation involves introducing new operators $\underline{O}_1{}';\underline{O}_2{}'\ldots\underline{O}_k{}'\ldots$ in place of $\underline{O}_1\ldots\underline{O}_k\ldots$ that are orthogonal[14] in the sense that $\mathrm{Tr}\underline{O}_k{}'\underline{O}_l{}' = 0; k \neq l$. In terms of these orthogonal operators $\underline{\tau}$ is diagonal and inversion of Eq. (27) becomes trivial, reducing considerably the time of each iteration. In addition, there are theoretical reasons to believe that the rate of convergence should be improved. We will return to this point later.

We write the constraints as usual in the form

$$\mathrm{Tr}\underline{P}\underline{O}_k = O_k\,. \tag{28}$$

We now introduce orthogonal operators via a Schmidt orthogonalization procedure. For example, let

$$\begin{aligned}
&\underline{O}_1{}' \equiv \underline{O}_1\,,\\
&\underline{O}_2{}' \equiv \underline{O}_1 + a_{22}\underline{O}_2\,,\\
&\underline{O}_3{}' = \underline{O}_1 + a_{23}\underline{O}_2 + a_{33}\underline{O}_3, \ldots\\
&\underline{O}_k{}' = \underline{O}_1 + \sum_2^k a_{\alpha k}\underline{O}_\alpha\,,
\end{aligned} \tag{29}$$

where $\mathrm{Tr}\underline{O}_k{}'\underline{O}_l{}' = 0;\ k \neq l$ serves to determine the parameters $a_{22} \cdots a_{kk}$. In this formalism, the Lagrange multipliers are given by

$$\lambda_k^{(n)} = (O_k{}' - \mathrm{Tr}\underline{\mathcal{P}}_n\underline{O}_k{}')/\mathrm{Tr}\underline{O}_k{}'^2\,, \tag{30}$$

where $O_k{}' = O_1 + a_{2k}O_2 + \cdots a_{kk}O_k$. The first-order iterative $\underline{P}$ equations now become

$$\underline{P}_{n+1} = \sum[(O_k{}' - \mathrm{Tr}\underline{\mathcal{P}}_n\underline{O}_k{}')/\mathrm{Tr}\underline{O}_k{}'^2]\underline{O}_k{}'. \tag{31}$$

One easily sees now that $\mathrm{Tr}\underline{P}_{n+1}\underline{O}_k{}' = \underline{O}_k{}'$, and therefore the constraints are identically satisfied at every iteration. In addition, we see that

$$\lambda_k^{(n)} \equiv (O_k{}' - \mathrm{Tr}\underline{\mathcal{P}}_n\underline{O}_k{}')/\mathrm{Tr}\underline{O}_k{}'^2 \to 0 \quad \text{as } n \to \infty,$$

since in that limit

$$\underline{\mathcal{P}}_n \equiv 3\underline{P}_n{}^2 - 2\underline{P}_n{}^3 \to \underline{P}_n\,.$$

Another practical advantage that we have realized is that, in every case tried, the number of iterations necessary for convergence is reduced. A possible reason for this is seen by considering the step length in our iteration process. In first order,

$$\delta I \equiv \delta\,\mathrm{Tr}\{[\underline{P}^2 - \underline{P}]^2 - \sum\lambda_k\underline{O}_k\}$$

is proportional to $\mathrm{Tr}(\underline{P} - \underline{\mathcal{P}} - \sum_k\lambda_k\underline{O}_k)^2$. Now if one begins with an idempotent guess, $\underline{P}_0 = \underline{\mathcal{P}}_0$ and the improvement in I is given by

$$\delta I \sim \sum_{kl}\lambda_k\lambda_l\,\mathrm{Tr}\underline{O}_k\underline{O}_l\,. \tag{32}$$

But a quadratic form achieves its extreme value when it is in diagonal form. If, then, the $\underline{O}_k$ operators are chosen orthogonal, i.e., if we use the previously defined $\underline{O}_k{}'$, we have

$$\delta I \sim \sum_k\lambda_k{}^2\,\mathrm{Tr}\underline{O}_k{}'^2\,. \tag{33}$$

TABLE I. Rates of convergence of the $\underline{P}$ equations from an initial null-matrix guess for: A. Nonorthogonal operators without steepest descent; B. Orthogonal operators without steepest descent; C. Orthogonal operators with steepest descent.

Method	Number of Iterations	$\mathrm{Tr}(\underline{P}^2 - \underline{P})^2$
A	2500	10^{-8}
B	463	10^{-8}
C	84	10^{-8}

Thus, the orthogonal choice of operators generates an optimum one-step improvement from an idempotent guess.

Further improvement of the convergence rate can be obtained by combining the orthogonal operator formalism with the steepest-descent procedure detailed in paper II. We have found that the use of orthogonal operators combined with the steepest-descent procedure of paper II is the best. Some preliminary convergence data are given in Table I for the ground electronic state of the HF molecule. Using electrostatic and virial theorem constraints, the calculation reported in paper II was repeated with several different $\underline{P}$ equation algorithms. The data seem to corroborate our theoretical considerations on convergence. A more thorough study of the factors affecting convergence and their optimization is now being pursued.

IV. CONCLUSION

In this paper we have developed all the formalism necessary to apply the $\underline{P}$ equations to constrained eigenvalue problems. We have also given calculations on the He atom and $H_2{}^+$ molecule that serve to corroborate the theoretical considerations. It was suggested that the method is ideally suited for constrained variational calculations.[2] In this connection either empirical or theoretical constraints may be used. As an example of the latter, we discussed the "pointwise" local-energy method, based on the fact that even very simple variational calculations yield rather reasonable local-energy curves. Thus constraining a variational calculation to give the correct local-energy at a point, or set of points, may not be overly traumatic and at the same time may result in a considerable computational advantage.

Finally, the $\underline{P}$ equations have been put in their optimum form by recasting the constraints in terms of orthogonal operators. This form of the equations, in addition to yielding considerable computational advantage, yields an explicit expression for the Lagrange multipliers resulting in a much more transparent iterative density-matrix equation. When coupled with the steepest descent procedure, an optimum computational form is obtained.

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[5] For reasons discussed in paper IV, these constraints have been symmetrized.

[6] The actual mechanics of extracting a normalized eigenvector from an idempotent $\underline{P}_i$ with Tr$\underline{P}_i < 1$ is simple. By virtue of the factorization $\underline{P}_i = \underline{C}_i \underline{C}_i^\dagger$, every column of $\underline{P}_i$ is proportional to $\underline{C}_i$. It is only necessary, then, to renormalize a given column of $\underline{P}_i$. On the other hand, one may choose to formulate the eigenvalue problem such that $\underline{P}^2 = \underline{P}$ and Tr$\underline{P} = n < m$. This implies that $\underline{P} = \underline{C}\,\underline{C}^\dagger$ where $\underline{C}$ is a rectangular matrix $(m \times n)$ containing n eigenvectors. This approach has the advantage of requiring the determination of fewer density matrices, but suffers in that an independent scheme for extracting the n eigenvectors is necessary.

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Many-Body Approach to Hyperfine Interaction in Atomic Nitrogen*

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The Brueckner-Goldstone many-body perturbation theory has been applied to calculate the hyperfine constant a of atomic nitrogen in its ground state ${}^4S_{3/2}$. The exchange core-polarization diagrams lead to contributions of $-49.710\,72$ and $55.418\,82$ Mc/sec from the 1s and 2s states, respectively, adding to a total of $5.708\,10$ Mc/sec. Higher-order diagrams characterizing mainly correlation effects produce an additional contribution of $4.780\,22$ Mc/sec. The total theoretical result 10.49 ± 0.15 Mc/sec is in excellent agreement with the experimental value of $10.45 \pm 0.000\,07$ Mc/sec. The major correlation effect arises from the interaction between the valence electrons and core s electrons, the effect of the 2s being the dominant one. It is found that a knowledge of the wave function up to second order is adequate for a sufficiently accurate evaluation of the hfs constant. The trends in the contribution from various physical effects observed by an analysis of pertinent diagrams are expected to be helpful in simplifying the analysis of more complex atoms.

I. INTRODUCTION

The Brueckner-Goldstone (BG) linked-cluster perturbation approach[1] to many-body theory has been applied successfully by Kelly[2,3] to the atomic systems beryllium and oxygen. The method was shown to yield excellent results for correlation energy, polarizabilities, and shielding factor. The BG theory was also used recently for calculation of the ground-state properties of atomic lithium by Chang, Pu, and Das.[4,5] In particular, Chang *et al.*[4] utilized this approach for the first time in a calculation of the hyperfine structure (hfs) constant of lithium atom ${}^2S$ and obtained good