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Direct Determination of Pure-State Density Matrices. I. Some Simple Introductory Calculations*

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A method is developed for the semiempirical determination of an electron density in small diatomic molecules. The method involves primarily the electrostatic and virial theorems and empirical potential curve data. The density has been determined, using Slater-type basis functions, for the molecules H_2^+ , H_2 , He_2 , Li_2 , and N_2 . Expectation values are calculated and compared to exact or Hartree-Fock values. A theoretical discussion of the semiempirical densities via a natural-orbital analysis is given. These analyses show that (a) the electrostatic and virial theorems are effective when used to determine unknown parameters in a first-order density but that (b) some additional means must be provided to ensure N representability.

I. INTRODUCTION

It is clear that if a sufficiently complete set of empirical data is available for an atomic or a molecular system, the electronic density could be determined experimentally. For example, one approach would be via experimental one-electron moments. Unfortunately very few of these moments are measurable for any real physical system. Nonetheless one may proceed with what is available experimentally and augment these data with theoretical conditions and physical intuition. In such an approach one must face such questions as: Is it possible to determine an electron density with a limited amount of experimental data and expect other independent properties of the density to be properly represented? Our answer to this question is a qualified yes. An elucidation of this latter statement is one of the facets of this series of papers.

It will be our purpose in this paper to introduce a semiempirical method for the approximate determination of $\rho(\vec{r}'; \vec{r}, \vec{R})$, the first-order reduced density kernel in a polyatomic molecule with nuclear position vectors represented by \vec{R} . The method is built around three ideas. These are: (1) Several theorems exist that constitute necessary conditions for $\rho(\vec{r}'; \vec{r}, \vec{R})$ to be derivable from an exact eigenstate of a many-electron Hamiltonian; (2) There exist experimental data that make these theorems practicable if used properly; (3) Finally, and most importantly, the mathematical apparatus necessary to implement (2) has, so far, proven to be within the capabilities of a relatively modest size computer.¹ Thus, providing that we can es-

tablish the utility of the method, the full power of the large machine remains to be exploited.

Before getting into the necessary formalism we will present a short summary of the methodology. Instead of requiring a large set of independent one-electron expectation values, we will use for the present only three expectation values and back these up with a good intuitive choice of the functional form of $\rho(\vec{r}'; \vec{r}, \vec{R})$. In this first paper we make use of two theorems, which are the electrostatic and virial theorems for diatomics. These relate various integrals, involving only the first-order density kernel, to the potential-energy function of a molecule. Since, for diatomic molecules, there exists a wealth of experimental potential-curve data from either spectroscopic or scattering experiments, the choice of the aforementioned theorems is most propitious. The central step in the method involves forcing the experimental energy curves on the density via these theorems. This process leads to integral equations involving $\rho(\vec{r}'; \vec{r}, \vec{R})$. These equations cannot be solved in general. However, choosing the form of $\rho(\vec{r}'; \vec{r}, \vec{R})$ so as to separate the spatial \vec{r} dependence from the parameter \vec{R} dependence leads to solvable equations that result in meaningful semiempirical densities. It will be our purpose in this first paper to present a method that can be applied to some of the simplest diatomic molecules.

It must be pointed out that the densities to be determined will be limited by two things: (1) the assumed functional form of $\rho(\vec{r}'; \vec{r}, \vec{R})$; and (2) the accuracy of the experimental data used as input. The first is by far the most serious limitation. In every case these limitations will be investigated

by the simple expedient of comparing our densities and expectation values with experimental and independently calculated theoretical values when available. The results are also analyzed via

natural orbitals and it is here that some enlightening results regarding semiempirical densities are unearthed.

II. BACKGROUND

In the next few paragraphs, we will present a brief resume of density-matrix theory, the electrostatic theorem, and the virial theorem. Since many very good discussions of all of these topics exist in the literature, we will concentrate only on those results we will need in the development of the methods for calculating $\rho(\vec{r}'; \vec{r}, \vec{R})$.

Accordingly, we define the first and second-order spinless density kernels for N -electron ν -atomic molecules:

$$\begin{aligned}\rho_1(\vec{r}_1'; \vec{r}_1, \vec{R}) &\equiv N \int \Psi^*(\vec{r}_1' s_1, \dots, \vec{r}_N s_N; \vec{R}) \Psi(\vec{r}_1 s_1, \dots, \vec{r}_N s_N) d^{3(N-1)} r d^N s, \\ \rho_2(\vec{r}_1' \vec{r}_2'; \vec{r}_1 \vec{r}_2, \vec{R}) &\equiv N(N-1) \int \Psi^*(\vec{r}_1' s_1, \vec{r}_2' s_2, \dots) \Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots) d^{3(N-2)} r d^N s.\end{aligned}\quad (1)$$

The first-order density kernel evaluated at $\vec{r}' = \vec{r}$, will be called the electron density and denoted by $\rho_1(\vec{r}, \vec{R})$. Our interest is in the more general function $\rho_1(\vec{r}'; \vec{r}, \vec{R})$ because we use the virial theorem, which involves the electronic kinetic energy and, as is well known, cannot be calculated from $\rho_1(\vec{r}, \vec{R})$ alone. We will also need the expressions for one- and two-body spinless expectation values. These are

$$\begin{aligned}\langle \Psi | \sum_i \hat{O}_i | \Psi \rangle &= \int [\hat{O}_1 \rho_1(\vec{r}_1'; \vec{r}_1, \vec{R})]_{\vec{r}_1' = \vec{r}_1} d^3 r_1, \\ \langle \Psi | \sum_{i \neq j} \hat{O}_{ij} | \Psi \rangle &= \int [\hat{O}_{12} \rho_2(\vec{r}_1' \vec{r}_2'; \vec{r}_1 \vec{r}_2, \vec{R})]_{\vec{r}_1' = \vec{r}_1, \vec{r}_2' = \vec{r}_2} d^3 r_1 d^3 r_2,\end{aligned}\quad (2)$$

where \hat{O}_i and \hat{O}_{ij} are arbitrary. Since the method to be developed concerns itself only with obtaining ρ_1 as an end result, the second-order kernel will not be considered further in these papers.

The first of the expressions we will use is the electrostatic theorem²

$$\vec{\nabla}_\alpha E(\vec{R}_1 \dots \vec{R}_\nu) = \int \vec{\nabla}_\alpha (-Z_\alpha / |\vec{r} - \vec{R}_\alpha|) \rho_1(\vec{r}, \vec{R}_1 \dots \vec{R}_\nu) d^3 r, \quad (3)$$

where $\vec{\nabla}_\alpha$ is the α th nuclear-coordinate gradient, $E(\vec{R}_1 \dots \vec{R}_\nu)$ is the electronic energy of the molecule, Z_α is the charge on the α th nucleus, and \vec{R}_α is the position vector of the α th nucleus.

The second theorem to be used is the virial theorem and is given by

$$\sum_\alpha \vec{R}_\alpha \cdot \vec{\nabla}_\alpha E(\vec{R}_1 \dots \vec{R}_\nu) + E(\vec{R}_1 \dots \vec{R}_\nu) = -T(\vec{R}_1 \dots \vec{R}_\nu), \quad (4)$$

where $T(\vec{R}_1 \dots \vec{R}_\nu) \equiv \langle \Psi | -\frac{1}{2} \sum_i \nabla_i^2 | \Psi \rangle$, which can be written

$$T(\vec{R}_1 \dots \vec{R}_\nu) = \int [-\frac{1}{2} \nabla^2(\vec{r}) \rho_1(\vec{r}'; \vec{r}, \vec{R}_1 \dots \vec{R}_\nu)]_{\vec{r}' = \vec{r}} d^3 r \quad (5)$$

and is seen to involve again only the first-order density kernel.

Both the virial and electrostatic theorems can be thought of as integral equations in ρ_1 . These equations, however, are not of any standard type because of the complicated form of ρ_1 . If, for example, ρ_1 were independent of the nuclear-position vectors³ then Eq. (3) would become a Fredholm equation of the first kind, e.g., in the case of a diatomic hydride molecule $A-H$, a one-center density about atom A yields for the electrostatic theorem

$$\vec{\nabla} E(\vec{R}) = \int \vec{\nabla} (-Z_B / |\vec{r}_A - \vec{R}|) \rho(\vec{r}_A) d^3 r_A. \quad (6)$$

Here \vec{r}_A and \vec{R} are measured from the point of view of atom A , and $\vec{\nabla} E(\vec{R})$ can be thought of as an experimentally known quantity. But, of course, such a form for ρ_1 is not compatible with other known results.⁴ Another, possibly more realistic, form is $\rho_1(\vec{r}, \vec{R}) = \rho_A(\vec{r}_A) + \rho_B(\vec{r}_B)$, which again gives a standard Fredholm-type integral equation. One could make this "separated-atom" density even more realistic by scaling; i.e., let $\rho_1(\vec{r}, \vec{R}) = \xi_A^3 \rho_A(\xi_A \vec{r}_A) + \xi_B^3 \rho_B(\xi_B \vec{r}_B)$. This density also yields a solvable integral equation provided the scale factors $\xi_A = \xi_A(\vec{R})$ and $\xi_B = \xi_B(\vec{R})$ are known. More will be said about this type of density later.

A further type of density that can be partially determined is of the form

$$\rho_1(\vec{r}, \vec{R}) = a(\vec{R}) [\rho_A(\vec{r}_A) + \rho_B(\vec{r}_B)] + a_{AB}(\vec{R}) \Psi_A(\vec{r}_A) \Psi_B(\vec{r}_B).$$

Provided the functions $\rho_A(\vec{r}_A)$, $\rho_B(\vec{r}_B)$, $a(\vec{R})$, and $a_{AB}(\vec{R})$ are known, the unknown functions $\Psi(\vec{r}_A)$ and $\Psi(\vec{r}_B)$

can be found by Fourier-inversion techniques. This follows because the unknown term in the electrostatic theorem, which is essentially $\int (\vec{r}_B/r_B^3) \Psi_A(\vec{r}_A) \Psi_B(\vec{r}_B) d^3r_A$, is just the convolution of the functions (\vec{r}_B/r_B^3) , $\Psi_B(\vec{r}_B)$ and $\Psi_A(\vec{r}_A)$. Similar considerations apply to the "overlap" term in the kinetic energy, viz., $\int \Psi_A(\vec{r}_A) G_B(\vec{r}_B) d^3r_A$, where $G_B(\vec{r}_B) \equiv -\frac{1}{2} \nabla^2(\vec{r}_B) \Psi_B(\vec{r}_B)$. Thus, if we denote the Fourier integral operator by \hat{F} , we have the well-known result that

$$\hat{F} \left[\int \frac{\vec{r}_B}{r_B^3} \Psi_A \Psi_B d^3r_A \right] = \hat{F} \left[\frac{\vec{r}_B}{r_B^3} \Psi_B \right] \hat{F}[\Psi_A], \quad \hat{F} \left[\int \Psi_A G_B(\vec{r}_B) d^3r_A \right] = \hat{F}[\Psi_A] \hat{F}[G_B]. \quad (7)$$

Therefore, if the function $E(R)$ is known, the Fourier transforms of Ψ_A and Ψ_B can be solved for and then inverted.

There are actually several other forms for ρ , that render Eqs. (3) and (4) standard-type integral equations. There are many difficulties with this type of approach, however. The first is that the solvable forms are not nearly as general as is desired. The second is that the experimental data are almost never in the most suitable analytical form (e.g., the Fourier transformation of potential-curve data would require special fitting). The purpose of discussing this approach has been to point out its existence and the difficulties incumbent upon its use.

The rest of this first paper will be devoted to a method that utilizes well-known basis functions (Ψ_A and Ψ_B in the previous example) and, therefore, aims at determining the \vec{R} -dependent parameters such as $a(\vec{R})$, $a_{AB}(\vec{R})$, and $\zeta(\vec{R})$. Another comment on the method we propose is best put as a question. Is it at all fruitful to seek directly an electron density without any knowledge of the quantum-mechanical origin of the density; that is, is the function we determine in any sense derivable from an N -body wave function? This problem is taken up in more detail in Sec. IV, where the natural orbitals of our semiempirical densities are calculated, and the occupation numbers are discussed. In anticipation of the discussion, we may remark that even though there is no built-in assurance that our semiempirical densities are N representable (i.e., derivable from an N -body wave function) they turn out to be not so bad in this respect which is, no doubt, a result of the choice of basis.

A final remark in concluding this part pertains to the anticipated efficacy of the kinetic energy and force operators in determining a good semiempirical density. In the first case, the average value of the kinetic-energy operator when empirically adjusted should, we expect, give a correct description of the "size" of the charge distribution. Just elementary quantum mechanics allows one to have some intuitive faith in this idea. In the second case, the force should give suitable directional characteristics ("shape") to ρ_1 once it has been empirically adjusted.⁵ Neither of these conditions alone nor together, however, is sufficient to assure a proper density in every sense. However, we feel that when these conditions are coupled with a good choice for the functional form of ρ , a reasonably good result will be obtained. The only way to prove this, of course, is by considerable testing. The rest of this paper will be devoted to verifying these hypotheses by direct numerical comparison of our results with those of other methods.

III. THE MOLECULES H_2^+ , H_2 , Li_2 , AND He_2

In this section we put forth the following first-order density kernel for H_2^+ , H_2 , and He_2 :

$$\begin{aligned} \rho_1(\vec{r}_1'; \vec{r}_1, \vec{R}) = & a(\vec{R}) \zeta^3(\vec{R}) [1s_A(\zeta \vec{r}_A') 1s_A(\zeta \vec{r}_A) + 1s_B(\zeta \vec{r}_B') 1s_B(\zeta \vec{r}_B)] \\ & + \frac{1}{2} a_{AB}(\vec{R}) \zeta^3(\vec{R}) [1s_A(\zeta \vec{r}_A') 1s_B(\zeta \vec{r}_B) + 1s_A(\zeta \vec{r}_A) 1s_B(\zeta \vec{r}_B')], \end{aligned} \quad (8)$$

where $a(\vec{R})$, $a_{AB}(\vec{R})$, and $\zeta(\vec{R})$ are parameters to be determined semiempirically. Also, $1s(r) = (\xi_{1s}/\pi)^{3/2} \times \exp(-\xi_{1s} r)$, where ξ_{1s} is the atomic variational scale. For Li_2 we try

$$\begin{aligned} \rho_1(\vec{r}'; \vec{r}, \vec{R}) = & \rho_{1s} + a(R) \zeta^3(R) [2s_A(\zeta \vec{r}_A') 2s_A(\zeta \vec{r}_A) + \dots] \\ & + \frac{1}{2} a_{AB}(R) \zeta^3(R) [2s_A(\zeta \vec{r}_A') 2s_B(\zeta \vec{r}_B) + \dots], \end{aligned} \quad (9)$$

where ρ_{1s} is the atomic inner-shell density which we assume to be unaffected. Also, $2s(\vec{r}) = (\xi_{2s}^5/3\pi)^{1/2} r \times \exp(-\xi_{2s} r)$, and again ξ_{2s} is the best atom scale.

These kernels are now inserted into the virial and electrostatic equations. Along with $\int \rho_1(\vec{r}, R) d^3r = N$ (the total number of electrons), we have enough conditions to determine the parameters $a(R)$, $a_{AB}(R)$, and $\zeta(R)$. Table I gives the pertinent experimental data used in these calculations. The resulting equations are simple although iterative because of implicit ζ dependence. They involve only kinetic-energy, overlap, and force integrals which are all evaluated by standard methods.⁶ The calculations were done at the equilibrium distance for H_2^+ , H_2 , and Li_2 , and at $R = 2.40$ a. u. for He_2 .

The density parameters are presented in Table II. The first encouraging result that can be noted is that a_{AB} is positive for the stable molecules H_2^+ , H_2 , and Li_2 , and negative for the unstable system He_2 . This is in agreement with Mulliken's⁷ idea of overlap density and bound molecules.

Another thing to note is that where a comparison is possible the semiempirical ζ is larger than the variational. The explanation of this result is simply that the energy put in via the virial is experimental and therefore larger in magnitude than the variational energy. The most efficient way to compensate for this

TABLE I. Pertinent empirical data (a. u.).

Molecule	R	$U(R)$
H ₂ ^a	1.4007	- 1.174
H ₂ ⁺	2.0031	- 0.603
Li ₂	5.051	-14.991
He ₂ ^b	2.4000	- 5.531

^aThe data for H₂, H₂⁺, and Li₂ were taken from G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

^bThe data for He₂ were taken from P. Phillipson, *Phys. Rev.* **125**, 1981 (1962).

TABLE II. Density parameters for H₂, H₂⁺, Li₂, and He₂.

Molecule	a	a_{AB}	orbital exponent ζ
H ₂	0.504	1.535	1.271
H ₂ ⁺	0.466	1.511	1.486
Li ₂	0.8793	0.4660	0.723
He ₂	1.049	-1.065	1.685

energy difference is with the scale factor and a concomitant tightening of the charge cloud. The next step in the analysis is to use $\rho_1(\vec{r}'; \vec{r}, \vec{R})$ to calculate other expectation values and compare them with the various theoretical calculations available. These results are given in Tables III-IV.

Consider the H₂ molecule first (Table III). Since in this case there are several wave functions for which the density has the same form as Eq. (8), we list in Table III the quantities $a(R)$, $a_{AB}(R)$, and $\zeta(R)$ for these also. Expectation values for the best available variational calculation (see footnote c of Table III) are given for comparison.

The poor values of $\langle z^2 \rangle$ and $\langle r^2 \rangle$ obtained from the Heitler-London and the unscaled molecular orbitals (MO) are considerably improved by the use of the Wang MO(ξ) and Weinbaum functions; the introduction of a scale factor in the orbital exponent contracts the charge distribution to nearly the correct "size" as measured by these operators. However, scaling does not improve the quadrupole moment which is a measure of the "shape" of the charge distribution around the internuclear axis (z axis) and is not affected by scaling alone. In a similar analysis of some of the variational densities in Table III, Karplus⁵ pointed out that the value of the shape-determining parameter a_{AB} is not large enough, i. e., there is not sufficient charge transfer to the overlap region. This is in agreement with the findings of Bader and Jones⁹ who showed that these variational densities do not generally yield electrostatic equilibrium. The results obtained with our semi-empirical density indicate that it strikes a better balance between "size" and "shape" of the charge distribution. This is a consequence of the fact that we constructed our density to satisfy both energy and electrostatic requirements. Thus, while our values of $\langle \xi \rangle$ and $\langle r^2 \rangle$ are now only a little lower than the variationally scaled ones, the improvement in $\langle 3z^2 - r^2 \rangle$ is significant. For any further improvement, we need to construct a density using a larger basis set and, in particular, to include p_z -type basis functions (which are concentrated along the internuclear axis). This causes the charge density in the overlap region to increase and, consequently, $\langle z^2 \rangle$ decreases. The H₂⁺ results (Table IV) show much the same behavior.

The Li₂ calculations are given in Table V. The balance between "size" and "shape" that our semi-empirical density attained in H₂ does not appear here. This is apparently due to the absence of p_z -type functions in the density. Corroborating evidence to this effect is the almost complete agreement between our expectation values and those obtained from the Bagus and Gilbert⁹ wave function which, like our density, does not include any s - p mixing. Also, in a study of the electronic structure of the lithium molecule, Ishiguro *et al.*⁸ showed that the quadrupole moment depends critically upon the use of p_z basis functions.

TABLE III. Density comparison in H₂ (a. u.).

Density	a	a_{AB}	ζ	$\langle \xi \rangle^a$	$\langle r^2 \rangle$	$\langle 3z^2 - r^2 \rangle$
Heitler-London ^b	0.638	0.961	1.000	2.521	3.460	0.697
Wang ^c	0.679	0.934	1.166	2.260	2.665	0.729
MO	0.570	1.141	1.000	2.519	3.454	0.644
MO ^d	0.597	1.193	1.197	2.218	2.543	0.665
Weinbaum ^e	0.630	1.100	1.193	2.228	2.566	0.691
Semiempirical	0.504	1.535	1.271	2.128	2.293	0.591
Kolos-Roothaan ^f				2.213	2.543	0.516

^a $\xi \equiv (r_A + r_B)/R$, $\langle r^2 \rangle$, $\langle z^2 \rangle$ measured from the middle of the molecule.

^bW. Heitler and F. London, *Z. Physik* **44**, 455 (1927).

^cS. Wang, *Phys. Rev.* **31**, 579 (1928).

^dC. A. Coulson, *Trans. Faraday Soc.* **33**, 1497 (1937).

^eS. Weinbaum, *J. Chem. Phys.* **1**, 593 (1933).

^fW. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 219 (1960).

TABLE IV. Density comparison in H_2^+ (a.u.)

Density	$\langle \xi \rangle$	$\langle 1/r_A \rangle$	$\langle r^2 \rangle$	$\langle 3z^2 - r^2 \rangle$
MO ($\zeta = 1.228$) ^a	1.763	0.832	2.895	1.489
Semiempirical	1.600	0.918	2.180	1.147
James ^b	1.667	0.852	2.438	0.946

^aL. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics with Application to Chemistry* (McGraw-Hill Book Co., Inc., New York, 1935).

^bH. M. James, *J. Chem. Phys.* **3**, 9 (1935).

TABLE V. Density comparison in Li_2 (a.u.)

Density	$\langle 1/r_A \rangle$	$\langle \xi \rangle$	$\langle r_A^2 \rangle$	$\langle z_A^2 \rangle$
Limited Hartree-Fock ^a	6.330	8.140	103.9	77.72
Bagus-Gilbert ^a	6.318	8.306	108.6	84.31
Semiempirical	6.363	8.203	106.6	85.62
Hartree-Fock ^a	6.337	8.113	103.0	78.47

^aUniversity of Chicago Molecular Physics Group (private communication).

In the case of He_2 (Table VI), the remarkable agreement between the semiempirical calculation and the simple MO is a consequence of two things: The experimental energy and the variational energy differ very little at this distance and the bases are essentially identical. The fact that both of these calculations are in very good agreement with the Hartree-Fock is probably also a consequence of the relatively small energy differences involved.

IV. NATURAL ORBITALS

As is well known, $\rho_1(\vec{r}'; \vec{r})$ is the kernel of a Hermitian integral operator $\hat{\rho}_1$, the eigenfunctions of which yield a diagonal representation of $\rho_1(\vec{r}'; \vec{r})$. That is, the diagonal expansion

$$\rho_1(\vec{r}'; \vec{r}) = \sum_k n_k \Phi_k^*(\vec{r}') \Phi_k(\vec{r}) \quad (10)$$

exists¹⁰ and the n_k are the eigenvalues of $\hat{\rho}_1$. Thus $\hat{\rho}_1 \Phi_k = n_k \Phi_k$ with $\langle k | l \rangle = \delta_{kl}$. The functions Φ_k were first discussed by Löwdin¹¹ and are known as natural orbitals. In terms of the matrix representation the equation $\underline{P} \underline{C}_k = n_k \underline{C}_k$ with $\underline{C}_k^\dagger \underline{C}_i = \delta_{ki}$ is the corresponding eigenvalue equation, and \underline{C}_k is the representative of Φ_k in any orthonormal basis.

For a spinless fermion density kernel the "occupation numbers" must be bounded as $0 \leq n_k \leq 2$, which is a necessary condition that

$$\rho_1(\vec{r}', \vec{r}) \equiv N \int \Psi^*(\vec{r}'_1 \vec{r}'_2 \dots \vec{r}'_N) \Psi(\vec{r}_1 \vec{r}_2 \dots \vec{r}_N) d^3r_2 d^3r_3 \dots d^3r_N$$

where Ψ is a proper N -body fermion wave function. ρ_1 is then said to be N representable.¹² The case where some of the n_k are equal to two, and the rest are zero, defines the closed-shell Hartree-Fock approximation. The Hartree-Fock eigenfunctions are therefore natural orbitals.

In the present work natural orbitals are of particular interest because our density is semiempirical and, therefore, fermion N representability is not assured. As a matter of fact, our densities yield negative occupation numbers. This undesirable feature will be rectified in later papers of this series.

In the case of the simple 1s densities calculated for H_2^+ , H_2 , and He_2 , the natural orbitals are seen to be just the symmetry orbitals

$$1s_{\sigma_g} \equiv (1s_A + 1s_B)/2^{1/2} (1 + S_{AB})^{1/2} \quad \text{and} \quad 1s_{\sigma_u} \equiv (1s_A - 1s_B)/2^{1/2} (1 - S_{AB})^{1/2}$$

where S_{AB} is the overlap integral. These are the only two linearly independent 1s functions having the appropriate symmetry properties. We then have

$$\hat{\rho}_1 \begin{pmatrix} 1s_{\sigma_u} \\ 1s_{\sigma_g} \end{pmatrix} = \begin{pmatrix} n_{\sigma_u} 1s_{\sigma_u} \\ n_{\sigma_g} 1s_{\sigma_g} \end{pmatrix}$$

or more explicitly, letting n denote either of the eigenvalues,

$$\int \{ a[1s_A(r_A)1s_A(r_A') + 1s_B(r_B)1s_B(r_B')] + \frac{1}{2} a_{AB}[1s_A(r_A)1s_B(r_B') + 1s_A(r_A')1s_B(r_B)] \} \\ \times \{ [1s_A(r_A') \pm 1s_B(r_B')] / 2^{1/2} (1 \pm S_{AB})^{1/2} \} d^3r' = n [1s_A(r_A) \pm 1s_B(r_B)] / 2^{1/2} (1 \pm S_{AB})^{1/2}. \quad (11)$$

From this equation one easily sees that n is given by

$$n = a(1 \pm S_{AB}) \pm \frac{1}{2} a_{AB} (S_{AB} \pm 1) \quad (12)$$

from which we note that

TABLE VI. Density comparison in He₂ (a.u.).

Density	$\langle 1/r_A \rangle$	$\langle \xi \rangle$	$\langle r_A^2 \rangle$	$\langle z_A^2 \rangle$
Limited Hartree-Fock ^a	1.060	1.433	3.954	3.265
Semiempirical	1.062	1.434	3.966	3.280
Hartree-Fock ^b	1.060	1.459	4.1111	3.344

^aThe density used in this calculation was $\rho = 2(1s_{\sigma_g})^2 + 2(1s_{\sigma_u})^2$.

^bM. Krauss, National Bureau of Standards, Washington, D. C. (private communication).

$$n_{\sigma_g} + n_{\sigma_u} = 2a + a_{AB} S_{AB} = N.$$

In Table VII are the occupation numbers for H₂⁺, H₂, and He₂. It is to be noted first of all that our n_{σ_u} values are negative in the cases of H₂ and H₂⁺.¹³ In He₂ no negative occupation numbers result, but $n_{\sigma_g} > 2$, which contradicts the rule for fermion density-matrix occupation numbers. In all three cases then the semiempirical density is not N representable, i. e., with our small bases there exists no proper fermion wave function which yields the empirical energy and force via the virial and Hellman-Feynman theorems.

It is clear that something must be done to rectify this situation. One could work directly with parameters in the wave function, thereby ensuring N representability, but this would lead to unnecessary numerical problems. We suggest that a density-matrix approach is better.¹⁴ This idea will be pursued in subsequent papers in this series.

CONCLUSIONS

The virial and electrostatic theorems have been used to obtain reasonably good semiempirical electron densities for several small molecules.

The methods reported in this first paper are to be viewed as introductory. The areas in which they are lacking are three: (1) We need overall

TABLE VII. Natural orbital occupation numbers for H₂, H₂⁺, and He₂.

Molecule	Density	n_{σ_g}	n_{σ_u}
H ₂	Heitler-London	1.96	0.04
	Wang	1.94	0.06
	MO	2.00	0.00
	Weinbaum	1.98	0.02
	Semiempirical	2.09	-0.09
H ₂ ⁺ ^a	MO	1.00	0.00
	Semiempirical	1.34	-0.34
He ₂	MO	2.00	2.00
	Semiempirical	2.15	1.85

^aSee Ref. (13).

better agreement with experiment or Hartree-Fock. (2) We need more conditions on the density so as to permit more flexible functional forms. (3) We need, finally, a numerically smooth way of ensuring that the density has more physical occupation numbers.¹⁵

In the following papers in this series we will address ourselves to all of these problems.

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¹All of the numerical work reported in this and the following papers II-V was carried out on an IBM 1620-II Computer at the Georgetown University Computation Center.

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