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Algebraic 1 Matrices and Radial Momentum Distributions from Hylleraas-Type Wave Functions. ^1S Ground States of He and He-Like Ions[*]

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Spin-free 1 matrices $\gamma(\vec{r}\,|\,\vec{r}\,')$'s are obtained in algebraic form from simple Hylleraas-type (HY) wave functions for the ^1S ground states of He and several He-like ions. The algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$'s are then Fourier transformed to momentum space in order to obtain radial momentum distributions $I_0(p)$'s. The analytical method developed here allows $I_0(p)$'s to be calculated in a direct manner from HY wave functions. Although the present emphasis is on the method rather than on the "goodness" of individual $I_0(p)$'s, results for the ^1S He and Li^+ ground states are obtained from six-term HY functions which incorporate 99.1 and 98.0%, respectively, of the correlation energy.

I. INTRODUCTION

The purpose of this paper is to develop an analytical method for evaluating radial momentum distributions from two-electron Hylleraas-type (HY) wave functions $\Psi(r_1, r_2, r_{12})$'s. This is accomplished by obtaining the corresponding (spin-free) first-order density matrix[1] $\gamma(\vec{r}\,|\,\vec{r}\,')$ in algebraic form. Then, $\gamma(\vec{r}\,|\,\vec{r}\,')$ is Fourier transformed to momentum space, as described by Benesch and Smith,[2] in order to obtain the radial momentum distribution $I_0(p)$. A secondary purpose of this paper is to apply the analysis to relatively simple (two-, three-, and six-term) HY functions for the ^1S ground states of He and He-like ions.

The extension of the algebraic density matrix method to N-electron HY and configuration interaction (CI) wave functions is pointed out in Sec. II. The problem of Fourier transforming a $\gamma(\vec{r}\,|\,\vec{r}\,')$ which explicitly contains angular functions is briefly discussed in Sec. III.

We stress here that the Fourier transformation of the algebraic 1 matrix will yield $I_0(p)$ to exactly the same accuracy with which the original HY function was determined.[3] This is to be contrasted with the Fourier transformation of the natural orbital (NO) expansion of $\gamma(\vec{r}\,|\,\vec{r}\,')$. Although the Fourier transformation of the NO's is accomplished exactly,[3] the NO expansion of a $\gamma(\vec{r}\,|\,\vec{r}\,')$ obtained from a HY function is necessarily truncated due to the problem of choosing a suitable *finite* basis set for expanding the NO's. In practice, this truncation error is very small. However, the determination of $\gamma(\vec{r}\,|\,\vec{r}\,')$ in algebraic form from a HY function eliminates the need for the NO expansion. The resulting $I_0(p)$ therefore does not incorporate *any* truncation error.

II. ALGEBRAIC EVALUATION OF $\gamma(\vec{r}\,|\,\vec{r}\,')$ FROM TWO-ELECTRON HY FUNCTIONS

As previously shown,[2] the radial momentum distribution $I_0(p)$ is obtained by Fourier transformation of the spin-free 1 matrix $\gamma(\vec{r}\,|\,\vec{r}\,')$ derived from a normalized N-electron wave function Ψ, namely,

$$I_0(p) = p^2 \int_0^{2\pi} \int_0^{\pi} \hat{\gamma}(\vec{p}\,|\,\vec{p}) \sin\alpha \, d\alpha \, d\beta$$

$$= p^2 \, \hat{\gamma}_0(p\,|\,p) \,. \tag{1}$$

The *diagonal* momentum-space 1 matrix is given[2] by

$$\hat{\gamma}(\vec{p}\,|\vec{p}) = (2\pi)^{-3} \int e^{-i\vec{p}\cdot(\vec{r}-\vec{r}\,')}\gamma(\vec{r}\,|\vec{r}\,')d\vec{r}\,d\vec{r}\,', \qquad (2)$$

where $\vec{p} = (p,\ \alpha,\ \beta)$ and $\vec{r} = (r,\ \theta,\ \phi)$; $\gamma(\vec{r}\,|\vec{r}\,')$ is the nondiagonal (spin-free) 1 matrix[1] in position space,

$$\gamma(\vec{r}\,|\vec{r}\,') = N \int \Psi(x_1,\ x_2,\ \ldots,\ x_n) \times \Psi^*(x_1',\ x_2,\ \ldots,\ x_n)ds_1(dx_i). \qquad (3)$$

In (3), x_i denotes the combined space and spin coordinates of electron i, $x_i = (\vec{r}_i,\ \eta_i)$, (dx_i) indicates integration over spatial coordinates and summation over spin variables of electrons 2 through N, while ds_1 means summation over the spin variable of electron 1. The subscript zero on $I_0(p)$ in (1) indicates that it only involves the spherically symmetric component (under spatial rotations) of $\hat{\gamma}(\vec{p}\,|\vec{p})$.

Since $\gamma(\vec{r}\,|\vec{r})$ is normalized in Löwdin's[4] convention to the number of electrons N, $\hat{\gamma}(\vec{p}\,|\vec{p})$ obtained from (2) is normalized in the same fashion,

$$\begin{aligned}\int \hat{\gamma}(\vec{p}\,|\vec{p})d\vec{p} &= (2\pi)^{-3} \int e^{-i\vec{p}\cdot(\vec{r}-\vec{r}\,')}\gamma(\vec{r}\,|\vec{r}\,')d\vec{p}\,d\vec{r}\,d\vec{r}\,' \\ &= \int \delta(\vec{r}-\vec{r}\,')\gamma(\vec{r}\,|\vec{r}\,')d\vec{r}\,d\vec{r}\,' \\ &= \int \gamma(\vec{r}\,|\vec{r})d\vec{r}\ . \end{aligned} \qquad (4)$$

We thus have a useful normalization check on computed $I_0(p)$ values, namely,

$$N = \int_0^\infty I_0(p)dp\ . \qquad (5)$$

Let us now specialize (3) to the case of a two-electron HY wave function $\Psi(r_1,\ r_2,\ r_{12})$ constructed for an atomic state of zero orbital angular momentum, i.e., a ${}^1S$ or ${}^3S$ state. The spin part of such a function is of no importance and we therefore dispense with it. The variational form chosen by Hylleraas[5] and others for functions of this sort is

$$\Psi(s,\ t,\ u) = \mathfrak{N}\ e^{-ks/2} \sum_{i,j,k} C_{i,j,k}\, s^i t^j u^k\ , \qquad (6)$$

where s, t, and u have their usual definitions, $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$. The constant $\mathfrak{N}$ is required for normalization.

As a first step in obtaining $\gamma(\vec{r}\,|\vec{r}\,')$ in algebraic form, we rewrite (6) explicitly as a function of r_1, r_2, and r_{12}. Since Ψ is real, (3) becomes

$$\gamma(\vec{r}\,|\vec{r}\,') = 2 \int \Psi(r,\ r_2,\ r_{12})\Psi(r',\ r_2,\ r_{12})d\vec{r}_2\ . \qquad (7)$$

In (7) and in the following analysis, $r \equiv r_1$ and $r' \equiv r_1'$.

The key to the algebraic 1 matrix analysis of $\Psi(r,\ r_2,\ r_{12})$ involves rewriting the volume element $d\vec{r}_2 = r_2^2 dr_2 \sin\theta_2 d\theta_2 d\phi_2$ as

$$d\vec{r}_2 = r_2^2 dr_2 r_{12} dr_{12} d\chi / r_2 r\ , \qquad (8)$$

where $0 \leqslant \chi \leqslant 2\pi$ is an angle of rotation about the position vector $\vec{r} = \vec{r}_1$. Details of this transformation are elementary and are described elsewhere.[6] We thus obtain[7,8]

$$\gamma(\vec{r}\,|\vec{r}\,') = (4\pi/r)\left\{ \int_0^r dr_2 r_2 \int_{r-r_2}^{r+r_2} dr_{12} r_{12}\, \Psi(r,\ r_2,\ r_{12})\, \Psi(r',\ r_2,\ r_{12}) + \int_r^\infty dr_2 r_2 \int_{r_2-r}^{r_2+r} dr_{12} r_{12} \Psi(r,\ r_2,\ r_{12})\, \Psi(r',\ r_2,\ r_{12}) \right\} \qquad (9)$$

after integrating over χ.[9]

With wave functions of the type given by (6), we have

$$\Psi(r,\ r_2,\ r_{12})\, \Psi(r',\ r_2,\ r_{12}) = e^{-k(r+r')/2}\, e^{-kr_2} \sum_{n,m} f_{nm}\,(r,\ r')r_2^n r_{12}^m\ . \qquad (10)$$

The *algebraic* coefficients f_{nm} collect various powers of r, r' in addition to products of expansion coefficients, the $C_{i,j,k}$'s in the original wave function (6). Equation (9) thus involves the integrals

$$I_{nm}(r) = \int_0^r dr_2\, r_2^{n+1}\, e^{-kr_2} \int_{r-r_2}^{r+r_2} dr_{12}\, r_{12}^{m+1} + \int_r^\infty dr_2\, r_2^{n+1}\, e^{-kr_2} \int_{r_2-r}^{r_2+r} dr_{12}\, r_{12}^{m+1}\ . \qquad (11)$$

For m even we obtain

$$I_{nm}(r) = J_{nm}(r)\ , \qquad (12)$$

whereas for m odd we have

$$I_{nm}(r) = J_{nm}(r) + K_{nm}(r)\ , \qquad (13)$$

where

$$J_{nm}(r) = \frac{2}{m+2} \sum_{j=1}^{m+2} \binom{m+2}{j} r^{m+2-j}\ \frac{(n+j+1)!}{k^{n+j+2}} \qquad (14)$$

and

$$K_{nm}(r) = \frac{2}{m+2}\, e^{-kr} \sum_{j=0}^{m+2} \sum_{i=0}^{n+j+1} (-1)^j \binom{m+2}{j} \times \binom{j+n+1}{i} \frac{i!}{k^{i+1}}\ r^{m+n+3-i}\ . \qquad (15)$$

In (14) and (15), $\binom{n}{m}$ denotes the binomial coefficient. The summation over j in (14) is to be carried out in *steps of two* while the summations over i and j in (15) are not restricted in this fashion.

Multiplication of the algebraic $f_{nm}(r, r')$'s in (10) by the appropriate $I_{nm}(r)$'s yields $\gamma(\vec{r}\,|\,\vec{r}\,')$ (Ref. 9) in the analytic form

$$\gamma(\vec{r}\,|\,\vec{r}\,') = e^{-k(r+r')/2} \sum_{\mu,\nu} A_{\mu\nu} r^{\mu} r'^{\nu} + e^{-3kr/2} e^{-kr'/2} \sum_{\mu,\nu} B_{\mu\nu} r^{\mu} r'^{\nu} . \qquad (16)$$

The A's and B's collect from the preceding analysis the algebraic coefficients for given powers μ and ν of r and r'.

Equation (16) was obtained assuming (6) for the variational form of the two-electron ^1S or ^3S Ψ. Other forms,[10] namely, those that incorporate different exponential parameters for r_1 and r_2 in the separable portion of $\Psi(r_1, r_2, r_{12})$, lead to expressions of similar type given in (14) and (15) for $J_{nm}(r)$ and $K_{nm}(r)$.

Although the above analysis was performed for spherically symmetric two-electron atomic states described by HY functions, it can be extended to many-electron atoms. For example, the spin-free second-order reduced density matrix (or 2 matrix) $\Gamma^{(2)}(\vec{r}_1, \vec{r}_2\,|\,\vec{r}_1\,', \vec{r}_2\,')$ can be constructed from the normalized N-electron wave function $\Psi(x_1, x_2, \ldots, x_n)$. Then, $\vec{r}_2\,'$ is set equal to $\vec{r}_2$. If the resulting $\Gamma^{(2)}$ contains the interelectron coordinate r_{12}, as will be the case if Ψ is of the HY type, the transformation given by (8) can be used to eliminate the r_{12} and r_2 dependence. If $\Gamma^{(2)}$ is independent of r_{12}, as will be the case if Ψ is of the usual configuration-interaction (CI) type, the labor involved in integrating out the coordinates of electron 2 is considerably simplified. In both cases an algebraic expression obtains for $[2/(N-1)]\,\gamma(\vec{r}\,|\,\vec{r}\,')$.

III. EVALUATION OF $I_0(p)$ FROM $\gamma(\vec{r}\,|\,\vec{r}\,')$

We will now evaluate (2) using the algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$ given by (16). Since $\gamma(\vec{r}\,|\,\vec{r}\,')$ in (16) is independent of angular functions, integration over (θ, ϕ) and (θ', ϕ') in (2) yields a factor $(4\pi)^2 j_0(pr) \times j_0(pr')$, $j_0(x) = (\sin x)/x$. The expression for $\hat{\gamma}(\vec{p}\,|\,\vec{p})$ thus reduces to a sum of products of radial integrals. These integrals involve powers of r (or r'), exponential terms and zero-order spherical Bessel functions, the j_0's. The diagonal 1 matrix in momentum space is thus given by

$$\hat{\gamma}(\vec{p}\,|\,\vec{p}) = (2/\pi)\Big[\sum_{n,m} A_{nm} R(\tfrac{1}{2}k, n+2, p)\, R(\tfrac{1}{2}k, m+2, p) + \sum_{n,m} B_{nm} R(\tfrac{3}{2}k, n+2, p)\, R(\tfrac{1}{2}k, m+2, p)\Big] , \qquad (17)$$

where the summation indices (n, m) in (17) replace (μ, ν) in (16). The radial integrals $R(z, i, p)$ appearing in (17) are explicitly defined as

$$R(z, i, p) \equiv \int_0^\infty e^{-zx} x^i j_0(px)\, dx . \qquad (18)$$

Various analytical expressions have been given for integrals of this type.[11]

In order to obtain $I_0(p)$, we integrate (17) over α and β, $\vec{p} = (p, \alpha, \beta)$. Since $\hat{\gamma}(\vec{p}\,|\,\vec{p})$ as given by (17) does not involve any functions of these angles, this integration yields a factor of 4π. Hence $I_0(p)$ is given by

$$I_0(p) = 4\pi p^2 \hat{\gamma}(\vec{p}\,|\,\vec{p}) = p^2\, \hat{\gamma}_0(p\,|\,p) , \qquad (19)$$

i.e., $\hat{\gamma}_0(p\,|\,p)$ is 4π times the expression given by (17).

Had $\gamma(\vec{r}\,|\,\vec{r})$ depended on the orientations as well as on the magnitudes of $\vec{r}$, $\vec{r}\,'$, the initial expression for $\hat{\gamma}(\vec{p}\,|\,\vec{p})$ would just involve the plane wave expansions for $e^{-i\vec{p}\cdot\vec{r}}$ and $e^{i\vec{p}\cdot\vec{r}\,'}$. The resultant expression for $\hat{\gamma}(\vec{p}\,|\,\vec{p})$ would then involve products of two (normalized) spherical harmonics, $Y_{lm}(\alpha, \beta)$'s; $\vec{p} = (p, \alpha, \beta)$. Integration over the spherical harmonics then yields $\hat{\gamma}_0(p\,|\,p)$.

In actual $I_0(p)$ calculations, it is recommended that the normalization condition stated in (5) be verified. Similarly, problems can be avoided if the algebraic expression for $\gamma(\vec{r}\,|\,\vec{r}\,')$ [or the NO expansion of $\gamma(\vec{r}\,|\,\vec{r}\,')$] is checked before it is Fourier transformed. This is most easily accomplished by setting $\vec{r}\,' = \vec{r}$, thereby yielding the diagonal matrix $\gamma(\vec{r}\,|\,\vec{r})$. Integration of $\gamma(\vec{r}\,|\,\vec{r})$ must then verify the normalization condition. A bonus feature of this check is that the radial electron-nuclear distribution function $D_0(r)$ is first obtained in analytical form from the algebraic $\gamma(\vec{r}\,|\,\vec{r})$, namely,

$$D_0(r) = r^2 \int_0^{2\pi} \int_0^{\pi} \gamma(\vec{r}\,|\,\vec{r}) \sin\theta\, d\theta\, d\phi , \qquad (20)$$

where

$$N = \int_0^\infty D_0(r)\, dr . \qquad (21)$$

Although the use of $\Psi(r', r_2, r_{12})$ rather than $\Psi(r', r_2, r_{12}')$ in (7) and (9) does not appear to affect $\gamma(\vec{r}\,|\,\vec{r}\,')$ significantly, the consequences are not immediately obvious. For the two-, three-, and six-term HY functions to be studied in Sec. IV, Eqs. (7) and (9) yield $\gamma(\vec{r}\,|\,\vec{r}\,')$'s whose corresponding $D_0(r)$'s, when integrated analytically, satisfy the normalization condition (21) to ten decimal places. The $I_0(p)$'s derived from the $\gamma(\vec{r}\,|\,\vec{r}\,')$'s, when numerically integrated, satisfy (5) to six or seven decimal places. Expectation values of the kinetic energy operator $-\frac{1}{2}\nabla^2$, obtained by operating on the algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$'s, are slightly smaller than those obtained by operating directly on the wave function $\Psi(r_1, r_2, r_{12})$ with $-\frac{1}{2}(\nabla_1^2 + \nabla_2^2)$. For ex-

TABLE I. Wave functions and energies of ^1S ground states of He and He-like ions.

Atom	Wave function	Energy $-E$(a.u.)	% corr.[a]
H$^-$	Two-term HY, No. 3 of Green *et al.* (Ref. 12)	0.508 78	52.3
	Three-term HY, No. 7 of Ref. 12	0.525 30	93.8
	Analytical RHF of Curl and Coulson (Ref. 13)	0.488 0	0[c]
	Exact[b]	0.527 751	100[c]
He	Two-term HY, No. 11 of Ref. 12	2.891 12	70.0
	Three-term HY, No. 14 of Ref. 12	2.902 62	97.4
	Six-term HY, Stewart and Webb (Ref. 14)	2.903 32	99.1
	CI, Table IV of Cressy, Miller, and Ruedenberg (Ref. 15), their ψ_3[d]	2.902 61[d]	97.4
	Best analytical RHF, Table VI of Roothaan, Sachs, and Weiss (Ref. 16)	2.861 680	0[c]
	Exact	2.903 724	100[c]
Li$^+$	Two-term HY, No. 16 of Ref. 12	7.268 15	73.0
	Three-term HY, No. 18 of Ref. 12	7.278 03	95.7
	Six-term HY, Stewart and Webb (Ref. 14)	7.279 06	98.0
	CI of Ahlrichs, Kutzelnigg, and Bingel (Ref. 17)	7.278 86[e]	97.6
	Analytical RHF, Table VI of Ref. 16	7.236 42	0[c]
	Exact[b]	7.279 913	100[c]
Be^{2+}	Three-term HY, No. 20 of Ref. 12	13.653 26	94.8
	Analytical RHF, Table VI of Ref. 16	13.611 30	0[c]
	Exact[b]	13.655 566	100[c]
B^{3+}	Three-term HY, No. 22 of Ref. 12	22.028 34	94.1
	Analytical RHF, Table VI of Ref. 16	21.986 23	0[c]
	Exact[b]	22.030 997	100[c]
C^{+4}	Three-term HY, No. 24 of Ref. 12	32.403 43	93.7
	Analytical RHF, Table VI of Ref. 16	32.361 19	0[c]
	Exact[b]	32.406 247	100[c]

[a] Percent of correlation energy is taken as %corr. = $[(E - E_{\mathrm{RHF}})/(E_{\mathrm{exact}} - E_{\mathrm{RHF}})] \times 100$, where E_{exact} is taken from Frankowski and Pekeris (Ref. 18); E_{RHF} is taken from Roothaan, Sachs, and Weiss (Ref. 16), except for H$^-$.

[b] Reference 18.

[c] By definition.

[d] While checking the He CI functions of Cressy, Miller, and Ruedenberg (Ref. 15) for normalization and other properties, ψ_3 and ψ_4 were found to have exactly the energy expectation values reported by these authors for ψ_4 and ψ_3.

[e] This energy is computed from a truncated version of Ahlrich, Kutzelnigg, and Bingel's (Ref. 17) CI function for Li$^+$. Further details of the truncated function and the respective $I_0(p)$ calculation are given in Ref. 2(c).

ample, the kinetic energy obtained by operating directly on the two-parameter He function of Green *et al.* (see Table I) is 2.918 32 a.u.; that calculated by operating on the algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$ is 2.861 68 a.u. Numerical integration of $I_0(p)$ weighted by the factor $\frac{1}{2}p^2$ gave 2.861 67 a.u. These small discrepancies for the kinetic energy will not be considered further at this time.

IV. RESULTS AND DISCUSSION

The analysis of Secs. II and III was applied to two- and three-term HY functions for the ^1S ground states of H$^-$, He, and Li$^+$. Three-term HY functions were employed for the ^1S ground states of Be^{2+}, B^{3+}, and C^{4+}. In addition, six-term HY functions were used for He and Li$^+$. The natural orbital (NO) expansions of $\gamma(\vec{r}\,|\,\vec{r}\,')$'s obtained from configuration interaction (CI) wave functions were also used to obtain correlated $I_0(p)$'s for He and Li$^+$; the CI results for Li$^+$ are those previously reported.[2(c)] Restricted Hartree Fock (RHF) $I_0(p)$'s were computed for H$^-$, He, Li$^+$, Be$^+$, B^{3+}, and C^{4+} by Fourier transformation of the respective RHF orbitals. Details of these various wave functions are collected in Table I.

The reduction of the various HY $\gamma(\vec{r}\,|\,\vec{r}\,')$'s to the algebraic form indicated in (16) was performed entirely by a program written in FORMAC.[19] The resulting algebraic expressions for the A's and B's of (16) were then incorporated into a FORTRAN IV program for further processing and subsequent evaluation of $I_0(p)$. Values of the A's and B's obtained from the algebraic 1 matrix analysis of the *six-term* HY function for the ^1S He ground state are given in Table II. The radial electron-nuclear distribution function obtained from this particular $\gamma(\vec{r}\,|\,\vec{r}\,')$ turns out to be

TABLE II. Algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$ from the six-term HY function for the ^1S He ground state.[a]

(n, m)[b]	A_{nm}[c]	(n, m)[b]	B_{nm}[c]
−1,0	0.518 335 0076	−1,0	−0.518 335 0076
−1,1	−0.968 708 8324 (−1)	−1,1	0.968 708 8324 (−1)
−1,2	0.329 744 5970 (−1)	−1,2	−0.329 744 5970 (−1)
0,0	0.224 575 4794 (+1)	0,0	−0.453 314 3855
0,1	−0.649 300 7026	0,1	0.117 313 6713
0,2	0.292 582 4964	0,2	−0.289 350 8838 (−1)
1,0	0.781 029 6234	1,0	−0.511 973 8405 (−1)
1,1	−0.874 349 9665 (−2)	1,1	0.378 020 8139 (−1)
1,2	0.117 458 3772 (−1)	1,2	0.0[d]
2,0	0.166 079 4212	2,0	−0.490 031 8376 (−1)
2,1	−0.653 209 6182 (−1)	2,1	0.0[d]
2,2	0.297 814 7215 (−1)	2,2	0.0[d]
3,0	0.706 599 7897 (−1)	3,0	0.0[d]
4,0	−0.812 221 9678 (−2)	4,0	0.0[d]

[a] Reference 14. The exponential parameter for this wave function is $k = 3.51$.

[b] These indices also indicate the powers of r and r', i.e., $r^n r'^m$, in expansion (16).

[c] Numbers in parentheses indicate powers of 10.

[d] The algebraic expressions for these particular coefficients are null.

$$D_0(r) = \sum_{n=1}^{6} a_n r^n e^{-kr} + \sum_{n=1}^{4} b_n r^n e^{-2kr} , \tag{22}$$

where the a's and b's are linear combinations of the A's and B's involved in $\gamma(\vec{r}\,|\,\vec{r}\,')$. As in a previous algebraic study[11a] of $D_0(r)$'s from HY wave functions, $a_1 = -b_1$. Table III lists for He the a's and b's implied by (22), and the computed norm of $D_0(r)$.

Table IV lists for selected values of p the $I_0(p)$'s obtained for the ^1S He ground state. Table V gives various $I_0(p)$'s for the ^1S ground states of H$^-$ and Li$^+$.[20] For details of the wave functions employed in these $I_0(p)$ computations, the reader is referred to the references in Table I. The $I_0(p)$'s reported in Tables IV and V were all integrated numerically and they all satisfy the normalization condition (5) with $N = 2$.

With the exception of the two-term HY $I_0(p)$, a cursory examination of Table IV indicates that the RHF, HY, and CI $I_0(p)$'s for the ^1S He ground state are in reasonably good agreement. Closer examination reveals that the correlated (three- and six-term HY) values are larger than the RHF values for $p = 0$–0.9, the peak maximum of each $I_0(p)$. One observes exactly the reverse behavior between the RHF and CI results. Disregarding the two-term HY values, the differences between RHF and correlated H$^-$ values are large enough that this ion should be investigated further, both theoretically and, if possible, experimentally.[21–24] If we again disregard the two-term results, we see from Table V that the correlated and RHF $I_0(p)$'s for Li$^+$ agree satisfactorily.

TABLE III. Distribution function $D_0(r)$ obtained from the algebraic $\gamma(\vec{r}\,|\,\vec{r}\,')$ of Table II. [$D_0(r) = 4\pi r^2 \gamma(\vec{r}\,|\,\vec{r})$, where $\gamma(\vec{r}\,|\,\vec{r})$ is obtained from $\gamma(\vec{r}\,|\,\vec{r}\,')$ by setting $r = r'$. See also Eq. (22). Numbers in parentheses indicate powers of 10; the computed norm of this distribution is "exactly 2.0, to ten decimal places.]"

n	a_n	n	b_n
1	0.651 358 9808 (+1)	1	−0.651 358 9808 (+1)
2	0.270 036 7162 (+2)	2	−0.447 920 1152 (+1)
3	0.206 972 3721 (+1)	3	0.416 472 4881
4	0.565 384 1586 (+1)	4	−0.504 366 2481
5	0.214 694 6182		
6	0.272 178 1938		

V. PRACTICAL CONSIDERATIONS INVOLVING THE ALGEBRAIC 1 MATRIX ANALYSIS

We have seen that the present analysis of the 1 matrix $\gamma(\vec{r}\,|\,\vec{r}\,')$ involves the manipulation of algebraic expressions according to a given prescription. Because these manipulations are algebraic and not merely numerical, they cannot be programmed for a digital computer in a language such as FORTRAN. In the present application, FORMAC[19] was chosen because it is an easy language to code.

Estimates of the computing time required to solve given problems are of particular importance. The FORMAC program currently in use is still in the development stage and has not been optimized to any extent. At present, its input is restricted to character strings composed of two-electron HY wave functions of the type shown in (6). For these and other reasons outlined below, no systematic effort has been made to obtain reliable time estimates for even the two-electron case. It is worth mentioning that 1.44 min of IBM 360 model 75 time were required to completely solve the six-term case for *both* He and Li$^+$.

At present, the author has reservations about the suitability of FORMAC for the algebraic 1 matrix

TABLE IV. $I_0(p)$'s for the ^1S ground state of He. The HY wave functions used for He and the He-like ions are of the form indicated in (6) and are given by $\Psi = \mathcal{N} e^{-\alpha s}(c_0 + c_1 u)$, $\Psi = \mathcal{N} e^{-\alpha s}(c_0 + c_1 u + c_2 t^2)$, $\Psi = \mathcal{N} e^{-\alpha s}(c_0 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2)$ for two-, three-, and six-term cases, respectively. Values of the various parameters for the two- and three-term wave functions are obtained from Ref. 12; the six-term He and Li^+ wave functions are given in Ref. 14.

p[a]	RHF	Two-term HY	Three-term HY	Six-term HY	CI
0.0	0.0	0.0	0.0	0.0	0.0
0.1	0.054 278	0.044 446	0.056 254	0.055 550	0.052 675
0.2	0.205 60	0.170 27	0.213 23	0.210 54	0.200 14
0.3	0.423 30	0.356 83	0.439 31	0.433 72	0.413 92
0.4	0.667 14	0.575 42	0.692 53	0.683 64	0.655 86
0.5	0.898 42	0.795 67	0.931 87	0.919 93	0.888 07
0.6	1.088 09	0.991 37	1.126 17	1.111 95	1.080 92
0.7	1.220 30	1.144 22	1.258 31	1.243 00	1.217 16
0.8	1.291 56	1.245 10	1.324 82	1.309 69	1.291 88
0.9	1.307 38	1.293 16	1.332 28	1.318 52	1.309 74
1.0	1.278 33	1.293 68	1.292 92	1.281 45	1.281 12
1.2	1.133 64	1.188 78	1.128 30	1.122 68	1.134 07
1.4	0.940 57	1.007 71	0.922 62	0.922 55	0.937 98
1.6	0.750 18	0.810 87	0.728 12	0.731 99	0.746 42
1.8	0.585 16	0.631 80	0.564 68	0.570 69	0.582 18
2.0	0.451 33	0.483 29	0.434 89	0.441 63	0.45010
3.0	0.123 57	0.121 95	0.121 29	0.124 85	0.126 74
4.0	0.038 684	0.035 469	0.038 460	0.039 699	0.040 344
5.0	0.014 025	0.012 244	0.013 955	0.014 406	0.014 640
10.0	0.000 375	0.000 301	0.000 367	0.000 378	0.000 383

[a] Linear momentum variable in reciprocal atomic units.

analysis. Any major programming effort should be undertaken with a view to producing a portable program. Portability of programs written in FORMAC is not realizable because the FORMAC compiler depends upon IBM's programming language, PL/1. Apart from the fact that FORMAC receives no support (it is issued as a Type III program by IBM), the current version is designed to run on IBM's 360 series, model 40 and above. As several possibilities regarding the computer implementation of the algebraic 1 matrix analysis remain to be explored, remarks concerning the best programming language, time estimates, and various computational procedures are best left to a future

TABLE V. $I_0(p)$'s for the ^1S ground states of H^- and Li^+.

	H^-			Li^+				
p[a]	RHF	two-term HY	three-term HY	RHF	two-term HY	three-term HY	six-term HY	CI
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	1.376 83	0.605 10	1.056 11	0.012 200	0.010 946	0.013 215	0.012 400	0.012 164
0.2	2.948 67	1.906 50	2.895 27	0.047 862	0.043 041	0.051 784	0.048 644	0.047 728
0.3	3.238 68	2.951 37	3.655 34	0.104 29	0.094 134	0.112 619	0.105 97	0.104 01
0.4	2.862 34	3.248 62	3.197 37	0.177 34	0.160 89	0.191 00	0.180 15	0.176 91
0.5	2.302 43	2.921 68	2.336 56	0.261 93	0.239 10	0.281 15	0.265 95	0.261 34
0.6	1.765 25	2.321 01	1.615 75	0.352 51	0.324 13	0.376 85	0.357 70	0.351 79
0.7	1.322 63	1.713 82	1.141 24	0.443 68	0.411 24	0.472 07	0.449 84	0.442 84
0.8	0.983 58	1.217 77	0.845 39	0.530 56	0.496 04	0.561 52	0.537 38	0.529 62
0.9	0.732 66	0.852 30	0.651 76	0.609 15	0.574 70	0.640 97	0.616 24	0.608 13
1.0	0.549 33	0.596 38	0.514 01	0.676 49	0.644 20	0.707 44	0.683 43	0.675 41
1.5	0.148 58	0.120 25	0.166 18	0.812 17	0.808 64	0.821 60	0.813 59	0.810 90
2.0	0.048 326	0.033 424	0.055 557	0.697 44	0.716 55	0.685 77	0.693 12	0.696 14
3.0	0.007 511	0.004 560	0.008 313	0.345 24	0.360 20	0.332 11	0.342 05	0.345 30
4.0	0.001 702	0.000 981	0.001 820	0.148 85	0.152 04	0.144 28	0.148 62	0.149 68
5.0	0.000 503	0.000 282	0.000 527	0.065 536	0.064 929	0.064 275	0.065 881	0.066 212
10.0	0.000 0093	0.000 0050	0.000 0094	0.002 591	0.002 334	0.002 579	0.002 603	0.002 623

[a] Linear momentum variable in reciprocal atomic units.

date.

On a more positive note, the algebraic analysis of the 1 matrix has definite advantages over the conventional NO analysis. First, for wave functions of the HY type, it is an exact method.[3] Second, the very real problem of choosing an appropriate set of basis functions (for the NO expansion) never arises. Third, and most important from the computational viewpoint, the algebraic analysis of the 1 matrix need be performed only *once* for *all* members of an isoelectronic sequence, provided that each member of the sequence is described by a wave function of the *same functional form*. This is easily seen if it is remembered that all parameters characterizing the given wave function are treated as *variables* during the algebraic analysis. After this analysis is completed, those wave-function parameters which characterize $\gamma(\vec{r}\,|\,\vec{r}')$ for a member of the sequence are assigned their appropriate values and evaluated by conventional methods (i.e., a FORTRAN program).

VI. SUMMARY

An analytical method has been developed which allows radial momentum distributions to be obtained directly from HY functions. The $I_0(p)$'s calculated for the ^1S ground states of He and He-like ions are primarily intended to illustrate the method. Further work, both experimental[25–29] and theoretical, will have to be performed in order to determine whether or not the CI and six-term HY $I_0(p)$'s actually represent an improvement over RHF. Although the two-, three-, and six-term HY functions are all energetically better than their RHF counterparts, differences between two- and three-term values for H^-, He, and Li^+ indicate that $I_0(p)$ is sensitive to both the accuracy and expansion length of the respective HY functions.

Whether or not the algebraic 1 matrix analysis is as practical for three-electron HY functions as it is for two-electron functions is an open question. The "best" HY function presently available for the Li atom[30] involves 100 terms. With FORMAC, the increased labor involved in reducing $\Psi\Psi^*$ to $\gamma(\vec{r}\,|\,\vec{r}')$ may prove more costly than the conventional NO expansion.[31] Problems of this sort are not anticipated when applying the analysis to two-electron HY functions.

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[1] The first-order reduced density matrix is often called the 1 matrix. As we are not concerned with spin, $\gamma(\vec{r}\,|\,\vec{r}')$ will simply be referred to as the 1 matrix rather than the charge-density matrix.

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[3] We differentiate possible errors in method from computational problems such as roundoff. For the latter reason, all numerical work performed on the IBM 360/75 at the University of Waterloo was done in double word arithmetic.

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[6] See, for example, C. A. Coulson and A. H. Neilson, Proc. Phys. Soc. (London) 78, 831 (1961); J.-L. Calais and P.-O. Löwdin, J. Mol. Spectry. 8, 203 (1962); H. Margeneau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, N. J., 1956), Vol. 1.

[7] Further details relating to the coordinate transformation (8) and to the limits of integration in (9) can be found in recent papers by the present author (see Ref. 8).

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[19] FORMAC (FORmula MAnipulation Compiler) is a high-level language that manipulates algebraic expressions. It was developed, but not supported, by IBM, and is now considered a dead language.

[20] More complete versions of Tables IV and V as well as the $I_0(p)$'s for Be^{2+}, B^{3+}, and C^{4+} will be supplied on request. Similarly, details of the algebraic $\gamma(\vec{r} \mid \vec{r}\,')$'s obtained from the two-, three-, and six-term HY functions, and the corresponding $D_0(r)$'s, will also be supplied.

[21] Compton profile studies for LiF indicate that a superposition of free-atom Li$^+$ and F$^-$ momentum densities represent the measured LiF density. By way of contrast, the valence-electron momentum distribution for LiH as obtained by Compton profile measurements [Ref. 22(b)] was found to be broader than that obtained from a superposition of free-ion H$^-$ and Li$^+$ densities. Similarily, the measured LiH valence-shell momentum distribution is broader than that calculated from crystal field wave functions [Ref. 22(b)]. Recently, Berggren and Martino (Ref. 23) obtained LiH Compton profiles from a tight-binding wave function and found that the calculated profile agreed ($\leq 10\%$) with the experimental profile [Ref. 22(b)], provided that the overlap between the hydrogen ions was taken into consideration. From self-consistent wave functions (with exchange) calculated in the cell approximation, Brandt (Ref. 24) obtained a LiH Compton profile and a valence-shell momentum distribution which only exhibited the dominant features of the measured [Ref. 22(b)] profile and valence-shell distribution.

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Multiconfiguration Self-Consistent-Field Theory for Localized Orbitals. I. The Orbital Equations*

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Variational equations are derived for the optimum orbitals for constructing a multiconfiguration expansion of the wave function for a many-electron system. Both the case where all Slater determinants are constructed from a common set of orbitals and the case where each determinant is constructed from an independent set of orbitals are considered. An equation with a single orbital operator is obtained in the former case; a separate operator for each determinant in the latter. The latter case corresponds to a physical picture in which the orbitals fluctuate as the system makes virtual transitions from one Slater determinant to another. The invariance properties of the wave function and of the variational equations with respect to linear transformations of the orbitals are analyzed, and various procedures are given for obtaining equations which select a unique set of orbitals. A prescription of Adams can be used in either case to localize the orbitals at a selected physical subsystem (an atomic shell, an atom, or a group of atoms). Another prescription can be used with a common set of orbitals to obtain an equation for natural spin orbitals.

I. INTRODUCTION

The invariance of the unrestricted-Hartree-Fock operator and wave function under orbital transformations was pointed out by Fock in his original work,[1] and first used by Hund to construct localized orbitals in molecules.[2] The invariance was also used by Wannier to construct the orthogonal localized orbitals which bear his name.[3] The theory of orthogonal localized orbitals was developed and used to interpret chemical concepts in a series of papers by Lennard-Jones and his collaborators.[4] These developments laid the ground work for a building-block approach to the theory of large molecules and solids. An important related development was the method of atoms in molecules developed by Moffit,[5] Hurley,[6] and Arai.[7] Hurley also derived equations for the localized orbitals in a wave function constructed from paired-electron orbitals.

Adams was the first to formulate a general self-consistent-field theory suitable for a building-block approach.[8] Reformulation of this theory in terms of pseudopotentials provided a useful tool for studying local properties of large polyatomic systems and for synthesizing wave functions for large