

Variational calculation of the single-particle density matrix and momentum density for the helium ground-state isoelectronic sequence*

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A recently developed variational formalism for the determination of the reduced single-particle density matrix, correct to second order, is applied to the ground state of the helium isoelectronic sequence. For a Slater-determinant-type trial wave function the method requires the initial determination of either the charge density or equivalently its cosine Fourier transform for spherically symmetric systems. The trial wave function employed is a one-parameter Hartree product of hydrogenic functions and use is made of the highly accurate analytic expressions derived elsewhere for the Fourier transform of the charge density for the helium sequence. Analytic expressions for the single-particle density matrix are obtained and the internal self-consistency of the technique with regard to the Kato cusp condition is discussed. These expressions are then employed to obtain closed form analytic expressions for the momentum density valid for the entire isoelectronic sequence. These results are subsequently employed to obtain expressions for the expectation values of the operators p^4 , p^2 , $|p|$, and $|p|^{-1}$ and the Compton profile in the impulse approximation. Analytic Hartree-Fock calculations for these properties are also performed, and the results of the variational calculation are compared with these results and those of many-parameter correlated wave-function calculations wherever possible. It is observed that the results of the single-parameter variational calculation for helium are highly accurate and improve further for each heavier element of the isoelectronic sequence.

I. INTRODUCTION

In a recent paper¹ we extended a variational formalism²⁻⁴ for obtaining expectation values, correct to second order, of Hermitian operators which may be written as a sum of single-particle operators, to the determination of the reduced single-particle density matrix, $\gamma(\vec{r}, \vec{r}')$, for an interacting many-electron system. The generalized reduced single-particle density matrix $\gamma_\zeta(\vec{r}, \vec{r}')$ is defined⁵ as

$$\gamma_\zeta(\vec{r}, \vec{r}') = N \sum_{\zeta_2 \dots \zeta_N} \int \psi^*(\vec{r}_1 \zeta_1, \vec{r}_2 \zeta_2, \dots, \vec{r}_N \zeta_N) \times \psi(\vec{r}' \zeta', \vec{r}_2 \zeta_2, \dots, \vec{r}_N \zeta_N) \times d\vec{r}_2 \dots d\vec{r}_N,$$

where ζ is the spin coordinate. The spinless form $\gamma(\vec{r}, \vec{r}')$ is given as

$$\gamma(\vec{r}, \vec{r}') = \sum_{\zeta} \gamma_\zeta(\vec{r}, \vec{r}').$$

The expectation value of the operator

$$Y = \sum_i Y_i = \sum_i W(\vec{r}_i) T_i(\vec{a}),$$

where $W(\vec{r}_i) = \delta(\vec{r}_i - \vec{r})$, $T_i(\vec{a})$ is a translation operator such that

$$T_i(\vec{a}) \psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_N) = \psi(\vec{r}_1, \dots, \vec{r}_i + \vec{a}, \dots, \vec{r}_N)$$

and where $\vec{a} = \vec{r}' - \vec{r}$ is $\gamma(\vec{r}, \vec{r}')$. The operator Y defined above, however, is not Hermitian, and no Hermitian operator exists whose expectation value yields $\gamma(\vec{r}, \vec{r}')$.¹ However, the expectation value of the complex operator X , defined as

$$X = Y + iZ,$$

is the reduced single-particle density matrix, where the Hermitian operators Y and Z are defined as

$$Y = \frac{1}{2} \sum_j [W(\vec{r}_j) T_j(\vec{a}) + W(\vec{r}'_j) T_j(-\vec{a})]$$

and

$$Z = -\frac{i}{2} \sum_j [W(\vec{r}_j) T_j(\vec{a}) - W(\vec{r}'_j) T_j(-\vec{a})].$$

Thus in order to obtain $\gamma(\vec{r}, \vec{r}')$ by the variational method we are required to calculate the expectation value of two Hermitian operators.

In general for a given choice of a Slater-determinant-type trial wave function, the determination of $\gamma(\vec{r}, \vec{r}')$ within this formalism requires the initial determination of either the electron charge density for the system or equivalently its cosine Fourier transform for spherically symmetric systems. These latter quantities are, however, derived by

the variational methods mentioned above for determining single-particle expectation values, as the expectations of the operators $W = \sum_i \delta(\vec{r}_i - \vec{r})$ and $U = \sum_i \cos(\vec{k} \cdot \vec{r}_i)$, respectively. The details of the technique in both the Hartree and Hartree-Fock approximations have recently been published.¹ In the present paper we present the results of an application of this formalism.

In Sec. II we apply this variational method to obtain expressions for the reduced single-particle density matrix correct to second order in the so-called two decoupling approximations^{3,4} as applied to the helium ground-state isoelectronic sequence. The trial wave function employed is a one-parameter Hartree product of hydrogenic functions and use is made of the highly accurate analytic expressions derived elsewhere^{6,7} for the Fourier transform of the charge density for the helium sequence. The internal self-consistency of the variational formalisms for obtaining single-particle expectation values and the single-particle density matrix is then discussed with regard to the satisfaction of the Kato cusp condition^{8,9} for the exact ground-state wave function of a two-electron system in the limit of coalescence of one electron with the nucleus.

Employing these expressions for the single-particle density matrix we derive in Sec. III closed-form analytic expressions for the momentum density valid for the entire isoelectronic sequence, and the results are compared with those of a six-parameter analytic Hartree-Fock wave function¹⁰ calculation. The results for the momentum density are then used to obtain closed-form analytic expressions for the expectation values of the operators p^4 , p^2 , and $|p|$ and a non-closed-form expression for the expectation value of $|p|^{-1}$, and these results are presented and compared with analytic Hartree-Fock calculations and correlated wave-function calculations due to Pekeris¹¹ wherever possible. Finally we calculate Compton profiles in the impulse approximation and compare our results for the helium ground state with those due to Hartree-Fock and a multiconfigurational self-consistent-field wave-function calculation.¹² In each of the above calculations the choice for the variational parameter is governed either by the energy-minimization criteria or by extremizing the property of interest.

II. APPLICATION TO THE HELIUM GROUND-STATE ISOELECTRONIC SEQUENCE

For the nonrelativistic two-electron system we write the Hamiltonian in atomic units as

$$H = H_0 + H',$$

where

$$H_0 = -\nabla_1^2 - \nabla_2^2 - 2Z_1/r_1 - 2Z_2/r_2$$

and

$$H' = 2(Z_1 - Z)/r_1 + 2(Z_1 - Z)/r_2 + 2/r_{12}$$

and choose the trial wave function ψ_{0T} to be a single-parameter product of hydrogenic functions:

$$\psi_{0T} = \prod_i \phi_i(\vec{r}_i) = (Z_1^3/\pi) e^{-Z_1(r_1+r_2)},$$

so that

$$H_0 \psi_{0T} = E_0 \psi_{0T}.$$

The Fourier transform of the charge density, or form factor, for the spherically symmetric two-electron system is the expectation value of the operator

$$U = \sum_{i=1}^2 U(k, r_i) = \sum_{i=1}^2 \frac{\sin kr_i}{kr_i}.$$

In the second decoupling approximation the form factor to second order is obtained by evaluating

$$\langle U \rangle \equiv F(k) = \bar{U} + (2/D) \text{Re} \langle \psi_{1T}^0 | H - E | \psi_{0T} \rangle,$$

where \bar{U} is the first-order expectation value

$$\bar{U} = \langle \psi_{0T} | U | \psi_{0T} \rangle$$

and⁷

$$D = 1 + \langle \psi_{1T}^1 | H - E | \psi_{0T} \rangle \\ = 1 + 3[(Z_1 - Z)/Z_1] + (2/Z_1)(\frac{19}{32} - \frac{3}{8} \ln 2),$$

and where $\psi_{1T}^0(v)$ and ψ_{1T}^1 are the auxiliary functions in the correction term. The additional subscript (U) in the auxiliary function, $\psi_{1T}^0(v)$ is used to indicate that it is the auxiliary function obtained specifically for the operator U . The function ψ_{1T}^1 is independent of the operator whose expectation value is being obtained.^{3,7} In all the results to follow if the factor D is set equal to unity we obtain the results in the first decoupling approximation.

In terms of the individual particle contributions to the total expectation value we rewrite $\langle U \rangle$ as

$$\langle U \rangle = \sum_{i=1}^2 [\bar{U}_i(k) + (2/D)F_i(k)],$$

where

$$\bar{U}_i(k) = \langle \psi_{0T} | U(k, r_i) | \psi_{0T} \rangle = 16Z_1^4 / (4Z_1^2 + k^2)^2,$$

and where $F_i(k)$ is the contribution of the i th particle to the correction term to \bar{U} (Ref. 7):

$$\begin{aligned}
F_i(k) &= \langle f_{iU}(k, r_i) \psi_{0T} | H - \mathcal{E} | \psi_{0T} \rangle \\
&= 2(Z_1 - Z) \left(-\frac{16Z_1^3 k^2}{A^3} \right) + \left[\frac{3Z_1^3}{A^2} \ln \frac{4A}{B} + \frac{3}{2} \left(\frac{Z_1^2(4Z_1^2 - k^2)}{kA^2} \right) \left(\tan^{-1} \frac{k}{4Z_1} - \tan^{-1} \frac{k}{2Z_1} \right) \right. \\
&\quad \left. - \frac{32Z_1^5(8Z_1^2 - k^2)}{A^2 B^2} + \frac{4Z_1^3(4Z_1^2 - k^2)}{A^2 B} + \frac{6Z_1^3}{AB} + \frac{32Z_1^5}{AB^2} - \frac{96Z_1^5}{A^2 B} - \frac{9Z_1^3}{2A^2} + \frac{10Z_1^3(4Z_1^2 - k^2)}{A^3} \right], \\
&\hspace{15em} A = (4Z_1^2 + k^2), \quad B = (16Z_1^2 + k^2).
\end{aligned}$$

$f_{iU}(k, r_i) \psi_{0T}$ is the i th component of the auxiliary function ψ_{1T}^0 . With the variational parameter Z_1 being chosen as the value which minimizes the energy, the results of the above analytic expression for the Fourier transform of the charge density are observed to be equivalent to the results of a 120-parameter configuration-interaction wave-function calculation,¹³ the maximum error over the entire momentum transfer range considered being 1.2% in the second decoupling approximation. The results also have an accuracy equivalent to that of an analytic Hartree-Fock wave-function calculation.¹⁴ It is expected therefore, owing to the unitary property of the Fourier transform, that the results for the single-particle density matrix, the momentum density, and properties in momentum space should prove to be quite accurate.

In terms of the components of the form factor, the single-particle density matrix correct to second order in the second decoupling approximation is given as¹

$$\begin{aligned}
\gamma(\vec{r}, \vec{r}') &= \gamma_0(\vec{r}, \vec{r}') + \gamma_1(\vec{r}, \vec{r}') \\
&= \sum_j \phi_j^*(\vec{r}) \phi_j(\vec{r}') \\
&\quad + \frac{1}{D} \sum_j \left(\phi_j^*(\vec{r}) \frac{J_j(\vec{r}')}{\phi_j^*(\vec{r}')} + \phi_j(\vec{r}') \frac{J_j^*(\vec{r})}{\phi_j(\vec{r})} \right),
\end{aligned}$$

where

$$J_j(\vec{r}) = \frac{1}{8\pi^3} \int F_j(\vec{k}) \cos \vec{k} \cdot \vec{r} \, d\vec{k}$$

is the cosine Fourier transform of the contribution of the j th particle to the correction term for the form factor $F_j(\vec{k})$ defined earlier. The results are

$$\gamma_0(\vec{r}, \vec{r}') = (2Z_1^3/\pi) e^{-Z_1(r+r')}$$

and

$$\begin{aligned}
\gamma_1(\vec{r}, \vec{r}') &= \frac{\gamma_0(\vec{r}, \vec{r}')}{D} \left[K(r) + K(r') - 3 \left(\frac{Z_1 - Z}{Z_1} \right) \right. \\
&\quad \left. - \frac{2}{Z_1} \left(\frac{19}{32} - \frac{3}{8} \ln 2 \right) \right],
\end{aligned}$$

where

$$\begin{aligned}
K(r) &= (Z_1 - Z)r + \frac{5}{8}r - \frac{1}{8Z_1} - \frac{1}{4Z_1} e^{-2Z_1 r} \\
&\quad - \frac{3(e^{-2Z_1 r} - 1)}{16Z_1 r} + \frac{3}{8} \int_0^{Z_1 r} \frac{e^{-2x} - 1}{x} dx.
\end{aligned}$$

The results in the first decoupling approximation are again obtained by setting the factor D equal to unity.¹⁵

The overall internal self-consistency of the variational formalism is most aptly demonstrated by the results of the second decoupling approximation. Since the charge density $\rho(\vec{r}) = \gamma(\vec{r}, \vec{r})$, it is possible to obtain from the above expression both the charge density at the nucleus $\rho(0)$ and its derivative at the nucleus $\lim(d\rho/dr)$ as $r \rightarrow 0$. It is then observed that the Kato cusp condition written in terms of these quantities and the atomic number

$$\lim_{r \rightarrow 0} \frac{d\rho(r)}{dr} = -2Z\rho(0),$$

is exactly satisfied and is independent of the parameter Z_1 . This result may also be demonstrated by obtaining $\rho(0)$ as the expectation value of the operator

$$W = \sum_{i=1}^2 \delta(\vec{r}_i)$$

and the derivative of the density at the origin from the infinite-momentum-transfer limit of the form factor

$$\lim_{k \rightarrow \infty} F(k) = \left(-8\pi \frac{d\rho}{dr} \Big|_{r=0} \right) \frac{1}{k^4},$$

provided of course the same trial wave function is used in the calculation of these expectation values.⁷

Since the results of the calculation of the expectation value of operators in configuration space via the density-matrix expressions derived above are equivalent to those obtained by calculating these expectations directly by the variational method, we now proceed to determine the momentum density and momentum-space expectation values.

III. CALCULATION OF MOMENTUM DENSITIES, EXPECTATION VALUES, AND COMPTON PROFILES

A. Momentum densities

In terms of the single-particle density matrix $\gamma(\vec{r}, \vec{r}')$, the density in momentum space is defined¹⁷ as

$$\rho(k) = \frac{k^2}{2\pi^2} \int e^{i\vec{k}\cdot\vec{r}} \gamma(\vec{r}, \vec{r}') e^{-i\vec{k}\cdot\vec{r}'} d\vec{r} d\vec{r}',$$

$$(\vec{p} = \hbar\vec{k}, \quad \hbar = 1).$$

$$\rho_1(k) = \frac{128Z_1^4 k^2}{D\pi R} \left[(Z_1 - Z) \left(\frac{4Z_1^3}{R^3} - \frac{1}{R^2} \right) + \frac{5Z_1^2}{2R^3} - \frac{9}{8R^2} - \frac{3}{4Q^2} + \frac{3}{2RQ} \right. \\ \left. - \frac{3}{16} \frac{(Z_1 - k^2)}{Z_1 k R} \tan^{-1} \frac{2kZ_1}{3Z_1^2 + k^2} + \frac{3}{16R^2} \ln \frac{R}{Q} - \frac{1}{R^2} \left[\frac{3}{2}(Z_1 - Z) + \frac{19}{32} - \frac{3}{8} \ln 2 \right] \right],$$

$$R = Z_1^2 + k^2, \quad Q = 9Z_1^2 + k^2.$$

We note that the above is a one-parameter closed-form analytic expression for the momentum density correct to second order valid for the entire iso-electronic sequence.

In Table I we present the results of the following calculations: $\rho_0(k)$, the first-order momentum distribution; $\rho^0(k)$ and $\rho(k)$, the momentum densities in the first and second decoupling approximations, respectively, for the energy-minimized value of Z_1 , viz. $Z_1 = Z - \frac{5}{16}$; and $\rho_{\text{HF}}(k)$, the results of a six-parameter analytic Hartree-Fock wave-function¹⁰ calculation.

We observe that our results in the two decoupling approximations are essentially equivalent to those due to analytic Hartree-Fock results for all values of the momentum k . This can be explained on the basis of the Brillouin-Moller-Plesset theorem¹⁸ as extended to the single-particle density matrix,¹⁹ thus leading to Hartree-Fock momentum densities and expectation values being correct to second order, as are our results, and hence the equivalence.

The improvement over the first-order momentum distribution $\rho_0(k)$ due to the addition of the correction term in the decoupling approximations is, however, substantial. In comparison with the Hartree-Fock results, for small values of momentum, say at $k=0.3$, $\rho_0(k)$ is in error by 20% while $\rho(k)$ differs from $\rho_{\text{HF}}(k)$ by 1.5%. At $k=0.5$, $\rho_0(k)$ is in error by 15.8% whereas $\rho(k)$ differs from $\rho_{\text{HF}}(k)$ by only 0.03%. The momentum distribution $\rho_0(k)$ does intersect the $\rho_{\text{HF}}(k)$ distribution at approximately $k=1$ and $k=3.4$, the error increasing between these values to 12.4% at $k=2$, whereas $\rho^0(k)$ differs from $\rho_{\text{HF}}(k)$ at this value by only 0.2%. With increasing momentum, this error in $\rho_0(k)$ is observed to increase further. Typically, at $k=6$,

On substitution of the expressions derived earlier for $\gamma(\vec{r}, \vec{r}')$ and on performing the above integration, the results for the momentum density in the second decoupling approximation are obtained as

$$\rho(k) = \rho_0(k) + \rho_1(k),$$

where $\rho_0(k)$ and $\rho_1(k)$ are the first-order and correction terms, respectively, and where

$$\rho_0(k) = 64Z_1^5 k^2 / \pi R$$

and

$\rho_0(k)$ is in error by 23.3%.

It is possible to determine the degree of accuracy of these different momentum distribution functions by calculating various expectation values of interest and comparing them to results of calculations of a many-parameter correlated wave-function calculation wherever possible.

B. Expectation values

With the momentum densities determined above we present analytical expressions for the expectation values $\langle W \rangle$ of the operators p^4 , p^2 , $|p|$, and $|p|^{-1}$ in the second decoupling approximation. The first term on the right-hand side of the expression for $\langle W \rangle$ below corresponds to \bar{W} , the first-order term, and the second to the correction term. The results reduce to those of the first decoupling approximation $\langle W \rangle_0$ if we set the factor D equal to unity. Since the expectation value is stationary^{1-3,7} with respect to arbitrary variations in the exact functions ψ_0 and ψ_1 , we also present below expressions for the variational parameter Z_1 which extremizes the expectation value in each decoupling approximation.

$$(a) \text{ For } W = p_1^4 + p_2^4,$$

$$\langle W \rangle = 10Z_1^4 + (128Z_1^3/D) \left[-\frac{5}{16}(Z_1 - Z) - \frac{33}{256} + \frac{3}{32} \ln 2 \right].$$

The extremum of $\langle k^4 \rangle_0$ occurs at

$$Z_1 = Z - \frac{3}{16} \left(\frac{11}{8} - \ln 2 \right).$$

The extremum of $\langle k^4 \rangle$ occurs at

$$Z_1 = Z - \frac{2}{3} \left(\frac{19}{32} - \frac{3}{8} \ln 2 \right).$$

$$(b) \text{ For } W = p_1^2 + p_2^2,$$

$$\langle W \rangle = 2Z_1^2 + (1/D) \left[-4Z_1(Z_1 - Z) - \frac{3}{4} Z_1 \right].$$

TABLE I. Momentum distributions for helium ground state. Here $\rho_0(k)$ is the first-order momentum distribution, and $\rho^0(k)$ and $\rho(k)$ the momentum densities in the first and second decoupling approximations, respectively. The variational parameter Z_1 is chosen such that $Z_1 = Z - \frac{5}{16}$. $\rho_{\text{HF}}(k)$ are analytic Hartree-Fock results.

k (a.u.)	$\rho_0(k)$	$\rho^0(k)$	$\rho(k)$	$\rho_{\text{HF}}(k)^a$
0.1	0.041 803	0.051 225	0.053 019	0.054 284
0.2	0.160 37	0.195 02	0.201 62	0.205 64
0.3	0.336 89	0.404 62	0.417 51	0.423 37
0.4	0.545 07	0.643 84	0.662 64	0.667 25
0.5	0.756 93	0.876 13	0.898 82	0.898 48
0.6	0.947 98	1.0722	1.0958	1.0880
0.7	1.1007	1.2140	1.2356	1.2201
0.8	1.2059	1.2955	1.3125	1.2913
0.9	1.2616	1.3198	1.3308	1.3071
1.0	1.2719	1.2962	1.3009	1.2782
1.1	1.2443	1.2368	1.2354	1.2166
1.2	1.1878	1.1535	1.1470	1.1338
1.3	1.1112	1.0568	1.0464	1.0394
1.4	1.0228	0.954 95	0.942 04	0.940 79
1.5	0.928 86	0.853 90	0.839 63	0.843 30
1.6	0.834 55	0.757 60	0.742 96	0.750 35
1.7	0.743 38	0.668 37	0.654 10	0.663 99
1.8	0.657 65	0.587 34	0.573 95	0.585 23
1.9	0.578 70	0.514 80	0.502 63	0.514 39
2.0	0.507 16	0.450 54	0.439 76	0.451 32
2.1	0.443 10	0.394 04	0.384 70	0.395 58
2.2	0.386 29	0.344 60	0.336 67	0.346 58
2.3	0.336 28	0.301 50	0.294 88	0.303 68
2.4	0.292 50	0.264 01	0.258 58	0.266 21
2.5	0.254 34	0.231 41	0.227 05	0.233 54
2.6	0.221 17	0.203 10	0.199 66	0.205 09
2.7	0.192 41	0.178 50	0.175 85	0.180 31
2.8	0.167 51	0.157 11	0.155 13	0.158 73
2.9	0.145 97	0.138 49	0.137 07	0.139 94
3.0	0.127 34	0.122 28	0.121 31	0.123 54
3.2	0.097 297	0.095 772	0.095 482	0.096 739
3.4	0.074 788	0.075 491	0.075 625	0.076 226
3.6	0.057 861	0.059 877	0.060 261	0.060 441
3.8	0.045 068	0.047 782	0.048 299	0.048 223
4.0	0.035 346	0.038 355	0.038 928	0.038 709
4.5	0.019 834	0.022 690	0.023 233	0.022 917
5.0	0.011 589	0.013 866	0.014 299	0.014 031
5.5	0.007 027 2	0.008 727 8	0.009 051 6	0.008 855 9
6.0	0.004 406 5	0.005 644 2	0.005 879 9	0.005 745 7

^aSee Ref. 10.

The extremum of $\langle W \rangle_0$ occurs at $Z_1 = Z - \frac{5}{16}$ which is the same value as that which minimizes the energy. The extremum of $\langle W \rangle$ occurs at

$$Z_1 = \frac{1}{64} [44Z + 5 - 20\mu + (405Z^2 + 288\mu Z - 112\mu^2 + 120\mu - 520Z + 25)^{1/2}],$$

where

$$\mu = \frac{19}{16} - \frac{3}{4} \ln 2.$$

(c) For $W = |p_1| + |p_2|$,

$$\langle W \rangle = \frac{16Z_1}{3\pi} + \frac{1}{D} \left(\frac{16}{3\pi} (Z - Z_1) + \frac{1}{\pi} \left(\frac{29}{6} + 4 \ln 2 - \frac{69}{8} \ln 3 \right) \right).$$

In this case $\langle W \rangle_0$ is independent of Z_1 . The extremum of $\langle W \rangle$ occurs at

$$Z_1 = \frac{1}{4} \{ 3Z - \mu + [Z^2 + (\frac{2}{3}\mu - 4\beta)Z + \frac{1}{3}\mu(4\beta - \mu)]^{1/2} \},$$

where

$$\mu = \frac{19}{16} - \frac{3}{4} \ln 2,$$

$$\beta = 3\pi\gamma/16,$$

$$\gamma = \frac{69}{8} \ln 3 - 4 \ln 2 - \frac{29}{6}.$$

(d) For $W = |p_1|^{-1} + |p_2|^{-1}$,

$$\langle W \rangle = \frac{32}{3\pi Z_1} + \frac{1}{D} \left(\frac{8\delta}{\pi Z_1^2} - \frac{32(Z - Z_1)}{3\pi Z_1^2} \right),$$

where

$$\delta = \frac{55}{48} + \ln 2 - \frac{75}{64} \ln 3 - \frac{3}{32} \lambda$$

and

$$\lambda = 8 \sum_{k=1}^{\infty} \frac{1}{(2k+1)^2} \frac{1}{2^{2k+1}}.$$

The extremum of $\langle W \rangle_0$ occurs at

$$Z_1 = Z - \frac{3}{4} \delta$$

and the extremum of $\langle W \rangle$ occurs at

$$Z_1 = \frac{4}{3} Z - (4\mu + 3\delta)/20 + \frac{1}{20} [16Z^2 + (12\mu - 51\delta)Z + 9\delta^2 + 9\mu\delta - 4\mu^2]^{1/2}.$$

Table II comprises results of the various calculations of the expectation value of the operators p^4 , p^2 , $|p|$, and $|p|^{-1}$ for the ground state of the helium atom. Included in this table are results due to (i) Pekeris,^{11,20} (ii) a six-parameter analytic Hartree-Fock wave-function calculation (HF),¹⁰ (iii) \bar{W} employing the trial wave function ψ_{0T} for the energy-extremized value of Z_1 (viz. $Z_1 = Z - \frac{5}{16}$), (iv) the results $\langle W \rangle_0$ of the first decoupling approxima-

TABLE II. Expectation values of the operators p^4 , p^2 , $|p|$, and $|p|^{-1}$ for the helium ground state. Here, \bar{W} is the first-order expectation value; $\langle W \rangle_0$ and $\langle W \rangle$ are the expectations in the first and second decoupling approximations with the value of the variational parameter Z_1 chosen to be $Z_1 = Z - \frac{5}{16}$; $\langle W \rangle_{0e}$ and $\langle W \rangle_e$ are the results obtained by extremizing the analytic expressions for the expectations in the first and second decoupling approximations with respect to the variational parameter Z_1 .

Calculation	Operator			
	p^4	p^2	$ p $	$ p ^{-1}$
Pekeris ^a	108.177	5.8074	•••	•••
HF ^b	105.865	5.7234	2.7990	2.1410
\bar{W}	81.0915	5.6953	2.8648	2.0120
$\langle W \rangle_0$	101.840	5.6953	2.8002	2.1224
$\langle W \rangle$	105.790	5.6953	2.7879	2.1434
$\langle W \rangle_{0e}$	103.917	5.6953	2.8002	2.1288
$\langle W \rangle_e$	103.856	5.6646	2.7864	2.1472

^aSee Ref. 11.

^bSee Ref. 10.

tion for $Z_1 = Z - \frac{5}{18}$, (v) the results of the second decoupling approximation $\langle W \rangle$ for $Z_1 = Z - \frac{5}{18}$, (vi) and (vii) the results of the first and second decoupling approximations $\langle W \rangle_{0e}$ and $\langle W \rangle_e$, respectively, for the value of Z_1 obtained by extremizing with respect to Z_1 the appropriate expressions $\langle W \rangle_0$ and $\langle W \rangle$.

Wherever possible we compare our results to those due to Pekeris. For the operator p^4 , we observe that for helium an error of 25% in \bar{W} is reduced to an error of 2.2% in $\langle W \rangle$ and that $\langle W \rangle_{0e}$ and $\langle W \rangle_e$ are in error by 4%. The analytic Hartree-Fock result is in error by 2.1% in this case. The essential equivalence of our results to those due to Hartree-Fock may, as described earlier, be understood on the basis of Brillouin's theorem. With each increase in atomic number this error is further decreased as expected. It is observed that for $Z = 8$, the error in $\langle W \rangle$ is reduced to 0.14% whereas \bar{W} is still in error by 5.4%. This improvement over the results of \bar{W} is also demonstrated for the case of the negative ion of atomic hydrogen H^- ($Z = 1$). In this case \bar{W} is in error by 54.6% whereas $\langle W \rangle$ is in error by only 7.8%. This is all the more interesting since with the same energy-minimized wave function a negative value is obtained for the electron affinity which we know must be positive since H^- is known to be stable.

For the kinetic energy operator p^2 , the correction term to \bar{W} vanishes for $Z_1 = Z - \frac{5}{18}$. Thus $\bar{W} = \langle W \rangle_0 = \langle W \rangle = \langle W \rangle_{0e}$ where the last equivalence is due to the fact that the value of Z_1 obtained by extremizing $\langle W \rangle_0$ is equivalent to that obtained by minimizing the energy. The vanishing of the correction term for $Z_1 = Z - \frac{5}{18}$ may be explained on the basis of the virial theorem,²¹ which states that for particles interacting through a Coulomb-force law,

$$\langle H \rangle = \frac{1}{2} \langle V \rangle = -\langle T \rangle,$$

where $\langle T \rangle$ is the average kinetic energy. Thus the error in the kinetic energy must be the same as that of the total energy obtained using an energy-minimized Hartree-product hydrogenic-type wave function, viz. 2% for helium.

The results due to Pekeris for the average value of the operators $|p|$ and $|p|^{-1}$ are unavailable and quantitative statements regarding the accuracy of our results cannot be made for these operators except that they are correct to second order. However, the trend of improvement of results for the expectation values as one lowers the power of the operator p would tend to lead to the conclusion that our results for the average values of $|p|$ and $|p|^{-1}$ are highly accurate. In comparison with the Hartree-Fock results for helium, \bar{W} for the operator $|p|$ differs by 2.3%, whereas $\langle W \rangle_0$ differs by 0.04%

and $\langle W \rangle$ by 0.4%. For $|p|^{-1}$, \bar{W} differs from the Hartree-Fock results by 6%, whereas typically $\langle W \rangle$ differs by 0.1% and $\langle W \rangle_e$ by 0.3%. It is also expected that these results improve further for each higher element of the isoelectronic sequence as was the case for the other operators. This certainly is borne out for the operator $|p|^{-1}$ in comparison with a Hartree-Fock²² calculation for the isoelectronic sequence where the latter results are obtained from Hartree-Fock calculations of the Compton profile function $J(q)$ (discussed in Sec. III C) since

$$\langle |p|^{-1} \rangle = 2J(0).$$

The results $\langle |p|^{-1} \rangle_{\text{HF}}$ for the isoelectronic sequence are as follows:

Z	$\langle p ^{-1} \rangle_{\text{HF}}$	Z	$\langle p ^{-1} \rangle_{\text{HF}}$
1	6.1328	5	0.7396
2	2.1424	6	0.6072
3	1.3112	7	0.5152
4	0.9460	8	0.4472

In comparison with $\langle |p|^{-1} \rangle_{\text{HF}}$ we observe that our results for $\langle W \rangle$ and $\langle W \rangle_e$ for $Z > 1$ are the same to three and four significant figures, the accuracy improving for the higher elements of the isoelectronic sequence. It is again interesting to note that in this case the results $\langle W \rangle$ for H^- differ by only 1.6%. Thus we do expect our results for the average value of $|p|^{-1}$ to be highly accurate. Typical experimental results for $J(0)$ for He are: x-ray scattering,²³ $1.066 \pm 0.7\%$; γ -ray scattering,²⁴ $1.071 \pm 1.5\%$; electron scattering,²⁵ $1.070 \pm 0.8\%$.

C. Compton profiles

Recently there has been a resurgence of interest in Compton scattering since it proves to be an effective microscopic probe of the momentum density of electronic systems.²⁶ In the so-called impulse approximation it is assumed that the interaction between the photon and electrons in the atoms takes place rapidly so that the electrons do not see a variable potential during the interaction. The Compton cross section from an atom containing many electrons in this approximation is given as²⁷

$$\frac{d\sigma}{d\Omega dE} = \left(\frac{d\sigma}{d\Omega} \right)_{\text{Th}} \frac{\omega_1}{\omega_2} J(q),$$

where $(d\sigma/d\Omega)_{\text{Th}}$ is the Thomson cross section, ω_1 and ω_2 the incident and scattered photon frequencies, and where $J(q)$ is the Compton profile function, defined as

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} \frac{\rho(k)}{k} dk$$

TABLE III. Compton profiles in the impulse approximation for the helium ground state. Here the $J_0(q)$ are the first-order Compton profiles, and $J^0(q)$ and $J(q)$ are the results in the first and second decoupling approximations, respectively, all the results being quoted for the value of the variational parameter Z_1 chosen such that $Z_1 = Z - \frac{5}{16}$. $J_{\text{HF}}(q)$ are the analytic Hartree-Fock results and $J_{\text{MC-SCF}}(q)$ the multiconfigurational self-consistent-field results.

q (a.u.)	$J_0(q)$	$J^0(q)$	$J(q)$	$J_{\text{HF}}(q)^b$	$J_{\text{MC-SCF}}(q)^a$
0.0	1.0060	1.0612	1.0717	1.0705	1.068
0.1	0.99549	1.0483	1.0583	1.0568	1.055
0.2	0.96479	1.0108	1.0195	1.0172	1.015
0.3	0.91636	0.95226	0.95909	0.95571	0.954
0.4	0.85385	0.87780	0.88236	0.87818	0.876
0.5	0.78157	0.79327	0.79550	0.79104	0.788
0.6	0.70389	0.70438	0.70447	0.70036	0.698
0.7	0.62480	0.61604	0.61437	0.61115	0.609
0.8	0.54760	0.53199	0.52901	0.52704	0.525
0.9	0.47474	0.45473	0.45092	0.45028	0.449
1.0	0.40783	0.38563	0.38140	0.38200	0.381
1.1	0.34773	0.32513	0.32083	0.32243	...
1.2	0.29472	0.27304	0.26892	0.27122	0.271
1.3	0.24864	0.22876	0.22497	0.22768	...
1.4	0.20906	0.19145	0.18811	0.19097	0.191
1.5	0.17537	0.16025	0.15737	0.16019	...
1.6	0.14691	0.13425	0.13184	0.13447	0.135
1.7	0.12299	0.11264	0.11067	0.11304	...
1.8	0.10297	0.094705	0.093131	0.095201	0.096
1.9	0.086267	0.079818	0.078590	0.080346	...
2.0	0.072351	0.067449	0.066516	0.067972	0.069
2.1	0.060769	0.057157	0.056469	0.057651	...
2.2	0.051131	0.048575	0.048088	0.049027	...
2.3	0.043109	0.041402	0.041007	0.041808	...
2.4	0.036426	0.035392	0.035195	0.035751	...
2.5	0.030852	0.030341	0.030244	0.030656	0.031
2.6	0.026195	0.026085	0.026065	0.026359	...
2.7	0.022297	0.022489	0.022525	0.022727	...
2.8	0.019029	0.019441	0.019519	0.019648	...
2.9	0.016283	0.016850	0.016959	0.017030	...
3.0	0.013969	0.014643	0.014771	0.014780	0.015
3.5	0.0067506	0.0075211	0.007677	0.0076065	...
4.0	0.0034697	0.0040766	0.0041922	0.0041300	...
4.5	0.0018852	0.0023152	0.0023971	0.0023519	...
5.0	0.0010757	0.0013697	0.0014257	0.0013962	...

^a See Ref. 12.

^b See Ref. 10.

with $q = \vec{K} \cdot \vec{p} / |\vec{K}|$ being the projection of the electron momentum \vec{p} on the scattering vector $\vec{K} = \vec{k}_1 - \vec{k}_2$, \vec{k}_1 and \vec{k}_2 being the initial and final photon momenta, respectively.

An analytic expression for $J(q)$ in the second de-

$$\begin{aligned}
 J(q) &= J_0(q) + J_1(q), \quad J_0(q) = 16Z_1^5 / 3\pi(q^2 + Z_1^2)^3, \\
 J_1(q) &= \frac{1}{\pi D} \left\{ \frac{Z_1^4 [3 + 4 \ln 2 - \frac{16}{3}(Z - Z_1)]}{L^3} + \frac{4Z_1^4 q^2 [8(Z - Z_1) - 5]}{L^4} + \frac{27}{32L} - \frac{23q^2}{32L^2} + \frac{73Z_1^2}{32L^2} - \frac{3}{8M} \right. \\
 &\quad + \left(\frac{11}{32Z_1^2} + \frac{2Z_1^4}{L^3} \right) \ln \left| \frac{L}{M} \right| + \frac{3 \tan^{-1}(q/Z_1)}{2Z_1^2} \left[2 \tan^{-1} \left(\frac{2qZ_1}{q^2 + 3Z_1^2} \right) - \tan^{-1} \left(\frac{q}{Z_1} \right) \right] \\
 &\quad \left. + \frac{q(3q^4 + 8Z_1^2 q^2 + 9Z_1^4)}{Z_1 L^3} \tan^{-1} \left(\frac{2qZ_1}{q^2 + 3Z_1^2} \right) - \frac{3(4 + \lambda)}{8Z_1^2} + \frac{9}{Z_1^2} I \left(\frac{q}{Z_1} \right) \right\},
 \end{aligned}$$

coupling approximation is given below, and as in the previous calculations the results of the first decoupling approximation may be obtained by setting the factor D to unity:

where

$$I(y) = \int_0^y \frac{\tan^{-1}x}{x^2+9} dx,$$

$$\lambda = 8 \sum_{k=1}^{\infty} \frac{1}{(2k+1)^2 2^{2k+1}},$$

$$L = (q^2 + Z_1^2), \quad M = (q^2 + 9Z_1^2).$$

In Table III we present results of various calculations of the Compton profile in the impulse approximation: $J_0(q)$, $J^0(q)$, and $J(q)$, the results of the first-order, first and second decoupling approximations with $Z_1 = Z - \frac{5}{16}$; $J_{\text{HF}}(q)$, the analytic Hartree-Fock results; and $J_{\text{MC-SCF}}(q)$, the multiconfigurational self-consistent-field calculations which incorporate non-Hartree-Fock correlation effects.

In comparison with the MC-SCF results for $q=0$, we observe that $J^0(0)$ and $J(0)$ differ by only 0.7% and 0.1%, respectively, and thus that $\langle |p|^{-1} \rangle_0$ and $\langle |p|^{-1} \rangle$ differ by the same percentage. In the range $0 < q < 1.2$, $J^0(q)$ and $J(q)$ differ by less than 1.3% and 1%, respectively. For the median range of q this difference never exceeds 3%. However, for

$q=3$, the results for $J^0(q)$ and $J(q)$ are exact to the accuracy quoted for the numerically obtained MC-SCF results. The improvement over the first-order calculations in each instance is substantial. It is also observed that $J^0(q)$ and $J(q)$ are essentially equivalent to the analytic Hartree-Fock results, being correct to two, and at times three, significant figures. Thus in this problem the effect of correlation proves to be fairly negligible. This conclusion tends to agree with the results of recent calculations for the helium²⁷ and neon^{28, 29} atom ground states that the effect of correlation on closed-shell systems appears to be negligible.

In conclusion, we note that together with the results presented in this paper and those in Refs. 2 and 4 we have applied variational methods for obtaining single-particle expectation values and the reduced single-particle density matrix, to derive for the helium ground-state isoelectronic sequence accurate, one-parameter, analytic expressions for all single-particle properties of interest in both configuration and momentum space. The study of other many-electron atoms by these variational methods is being pursued.

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