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Analytic Calculation of the Coherent Atomic Scattering Factor for the Ground State of the Helium Isoelectronic Sequence*

V. Sahni†
Department of Physics, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

and

J. B. Krieger‡
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

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The analytical method developed by the authors for the determination of the expectation value of single-particle operators $W=\sum_i W(\vec{r}_i)$ correct to second order is employed in both the first and second decoupling approximations to obtain analytic expressions for the coherent x-ray scattering factor $F(\vec{k})$ for the ground state of the helium isoelectronic sequence valid for all values of momentum transfer. The trial wave function ψ_{0T} employed is an energy-minimized Hartree product of hydrogenic states. For helium the results for the form factor in the second decoupling approximation are found to be superior to those of the first, and are within 1.2% of the highly accurate values calculated using a 120-parameter configuration-interaction wave function and have an accuracy equivalent to that of an analytical Hartree-Fock treatment. This error is further reduced as the atomic number is increased. In order to demonstrate the internal self-consistency of the technique, we prove that the expectation value of any single-particle operator as obtained by direct use of the analytical method is the same as the expectation value obtained employing the form factor provided that the latter has also been calculated by the analytical method employing the same trial wave function. Finally, we extend our calculations to the infinite-momentum-transfer range and study our results in this limit by employing a cusp condition for the exact ground-state wave function of two-electron atomic systems written in terms of the logarithmic derivative of the electron density at the origin. We observe that in the infinite-momentum-transfer limit our results for helium are in error by 0.57% and that this error is further diminished for each successive element of the isoelectronic sequence. In addition, we note that the cusp condition is exactly satisfied via the formalism of the second decoupling approximation and is independent of the variational parameter employed.

I. INTRODUCTION

The highly accurate results obtained via the analytic method[1,2] developed by the authors for the determination of the expectation value correct to second order of radially dependent single-particle operators

$$W(\vec{r}_1, \ldots, \vec{r}_N)=\sum_i W(r_i)$$

further motivate one to a calculation of the complete charge density of a spherically symmetric atom as a function of the continuous radial variable r. However, during the course of the investigation it was determined that it is analytically simpler to obtain instead the Fourier transform of the electron density.

The Fourier transform of the electron density is, however, exactly equivalent to the coherent x-ray scattering form factor which for an N-electron system is defined as

$$F(\vec{k})=\sum_{i=1}^{N} \langle\psi_0|\, e^{i\vec{k}\cdot\vec{r}_i}\,|\psi_0\rangle \quad , \tag{1}$$

where ψ_0 is the ground-state wave function, $\vec{r}_i$ is the radius vector from the nucleus to the ith electron, and $\vec{k}(\hbar=1)$ is the momentum transfer. The coherent scattering form factor is of importance first in the theory of scattering,[3] where it is related to (i) the differential cross section for coherent scattering of photons by an atom in lowest-order time-dependent perturbation theory via

$$\frac{d\sigma_{\mathrm{coh}}}{d\Omega}=I_{\mathrm{Th}}|F(\vec{k})|^2 \quad ,$$

where I_{Th} is the Thomson cross section for scattering of radiation by a free electron, and (ii) to the differential cross section for elastic scattering of charged particles by an atom in the first Born approximation via the relationship

$$\frac{d\sigma_{\mathrm{elastic}}}{d\Omega}=\left(\frac{2}{a_0 k}\right)^2 |Z-F(\vec{k})|^2 \quad ,$$

where a_0 is the Bohr radius and Z the number of protons in the nucleus. In addition, the coherent form factor, being the Fourier transform of the electron density, is of further importance as it may be employed in the determination of the expectation value of any nondifferential single-particle operator $W=\sum_i W(\vec{r}_i)$.

Now for a spherically symmetric atom the

Fourier transform of the electron density may be written as

$$\int e^{i\vec{k}\cdot\vec{r}}\,\rho(\vec{r})\,d\vec{r}=\int \rho(r)[(\sin kr)/kr]\,d\vec{r}\quad , \tag{2}$$

where $\rho(r)$ is the electron density. This implies that the form factor $F(\vec{k})$ as defined above is just the expectation value of the operator W, where W is given by

$$W=\textstyle\sum_i\,(\sin kr_i)/kr_i\quad . \tag{3}$$

As W may be written as a sum of single-particle operators dependent on the radial distance only, our technique for the determination of the expectation value of single-particle operators is immediately applicable.

In this paper we begin, after briefly reviewing the analytical method to be employed, by determining in Sec. II an analytical expression for the coherent x-ray scattering factor $F(\vec{k})$ for the ground state of the helium isoelectronic sequence valid for *all* values of momentum transfer $\vec{k}$ and for *all* elements of the isoelectronic sequence. As in the case of our previous[1] work on the expectation values of other operators for the ground state of helium (henceforth referred to as I) we choose our trial wave function ψ_{0T} to be an energy-optimized product of hydrogenic states. On comparison of our results for helium with those in the literature we find that our results are equivalent to the analytic Hartree-Fock values of Kim and Inokuti[4] and no more than 1.2% in error over the entire momentum-transfer range considered when compared with the highly accurate results of a 120-term configuration-interaction wave-function treatment due to Brown.[5] The results for the other elements of the isoelectronic sequence are found to improve consistently for each increase in the nuclear charge Z. We thus find that employing the technique discussed in the previous paper, highly accurate results for the form factor may be obtained without the necessity of employing very precise wave functions.

In Sec. III we prove the theorem that the expectation value of any radially dependent single-particle operator $W=\sum_i W(r_i)$ as obtained by direct use of the analytical method involving the specific W in question is entirely equivalent to the expectation value of the operator derived using the $F(\vec{k})$ obtained here provided that in both cases the same ψ_{0T} is employed. This theorem not only demonstrates the internal self-consistency of the technique but also enables us to discuss and compare our results for both small and large k limits more meaningfully with those existing in the literature. The above equivalence in the determination of $\langle W\rangle$ via the two formalisms thus implies that it is now possible to rederive all the results obtained in I. In order to be more specific we give in addition in Sec. III explicit analytic expressions for the expectation values of the operators discussed in I, namely, $r^n, n=-2,-1,1,2$, and the electron density at the origin in terms of the coherent form factor $F(\vec{k})$.

Finally we derive an analytic expression for the form factor for the ground state of the helium isoelectronic sequence in the infinite-momentum-transfer range. Results due to Brown and Kim and Inokuti are unavailable in this momentum-transfer range and the only method by which we may discuss the accuracy of our results is via a cusp condition due to Kato[6] describing the behavior of the exact wave function of a two-electron atomic system in the limit of coalescence of one of the electrons with the nucleus. In addition it is interesting to note that this cusp condition is exactly satisfied via our formalism and is also independent of the variational parameter employed.

II. APPLICATION OF TECHNIQUE AND RESULTS

We begin by briefly reviewing the analytical method developed in the preceding paper,[2] to be employed here in the determination of the coherent form factor for the ground state of a two-electron atom. For operators which may be written as a sum of single-particle operators dependent on the radial coordinate,

$$W=\textstyle\sum_i W(r_i)\quad , \tag{4}$$

the expectation value of W correct to second order is given by the expression

$$\langle W\rangle=\overline{W}+\frac{2\,\mathrm{Re}\int\psi_{1T}^{0*}(H-E)\,\psi_{0T}\,d\tau}{1+\mathrm{Re}\int\psi_{1T}^{1*}(H-E)\,\psi_{0T}\,d\tau}\quad , \tag{5}$$

where ψ_{0T} is a trial wave function which is assumed to be a Hartree product of single-particle wave functions of the form $\prod_i\varphi_i(\vec{r}_i)=\prod_i\varphi_i(r_i)Y_l^m(\theta_i,\varphi_i)$, $\overline{W}$ is the expectation value of the operator W using the trial wave function, i.e., $\int\psi_{0T}^{*}W\psi_{0T}\,d\tau$, H is the Hamiltonian, E is the energy of the system, and ψ_{1T}^{0} and ψ_{1T}^{1} are auxiliary functions defined by the relations

$$\psi_{1T}^{0}=\textstyle\sum_i f_i^0(r_i)\psi_{0T}\quad , \tag{6}$$

$$\psi_{1T}^{1}=\textstyle\sum_i f_i^1(r_i)\psi_{0T}\quad , \tag{7}$$

where $f_i^0(r_i)$ and $f_i^1(r_i)$, respectively, satisfy the second-order differential equations

$$\frac{d}{dr_i}\left(r_i^2\,\frac{df_i^0(r_i)}{dr_i}\right)+2r_i^2\,\frac{df_i^0(r_i)}{dr_i}\,\frac{d\phi_i(r_i)}{dr_i}\,\frac{1}{\phi_i(r_i)}$$

$$= r_i^2[W(r_i) - \overline{W}_i] \ , \qquad (8)$$

$$\frac{d}{dr_i}\left(r_i^2 \frac{df_i^1(r_i)}{dr_i} \right) + 2 r_i^2 \frac{df_i^1(r_i)}{dr_i} \frac{d\phi_i(r_i)}{dr_i} \times 1/\phi_i(r_i) = r_i^2 \ . \qquad (9)$$

The solutions of the two differential equations (8) and (9) are

$$f_i^0(r_i) = \int^{r_i} [r_i'^2 \phi_i^2(r_i')]^{-1} \{ \int_\infty^{r_i'} r_i''^2 \phi_i^2(r_i'')[W(r_i'') - \overline{W}_i] dr_i'' \} dr_i' + C_1 \ , \qquad (10)$$

$$f_i^1(r_i) = \int^{r_i} [r_i'^2 \phi_i^2(r_i')]^{-1} [\int_\infty^{r_i'} r_i''^2 \phi_i^2(r_i'') dr_i''] dr_i' + C_2 \ , \qquad (11)$$

where the constants C_1 and C_2 are chosen so as to orthogonalize the auxiliary functions ψ_{1T}^0 and ψ_{1T}^1 to ψ_{0T} in order to eliminate the generally unknown energy E from Eq. (5).

We now apply the procedure to determine the Fourier transform of the charge density for the ground state of the helium isoelectronic sequence. This, as mentioned earlier, is the expectation value of the operator

$$W = \sum_{i=1}^{2} (\sin kr_i)/kr_i \ . \qquad (12)$$

As our trial wave function ψ_{0T} we choose an energy-optimized simple product of single-particle hydrogenic wave functions

$$\psi_{0T} = \phi_1(r_1)\,\phi_2(r_2) = (Z_1^3/\pi)\, e^{-Z_1(r_1+r_2)} \ , \qquad (13)$$

where $Z_1 = Z - \frac{5}{16}$ and Z is the atomic number. The choice of a real ψ_{0T} leads to real auxiliary functions ψ_{1T}^0 and ψ_{1T}^1 as well. We write the Hamiltonian for the two-electron system in atomic units as

$$H = H_0 + H' \ ,$$

where

$$H_0 = -\nabla_1^2 - \nabla_2^2 - 2Z_1/r_1 - 2Z_1/r_2 \ ,$$
$$H' = 2(Z_1 - Z)/r_1 + 2(Z_1 - Z)/r_2 + 2/r_{12} \ , \qquad (14)$$

so that

$$H_0 \psi_{0T} = E_0 \psi_{0T} \ . \qquad (15)$$

Now

$$\overline{W} = \int \psi_{0T} W \psi_{0T} d\tau = 32 Z_1^4/(4Z_1^2 + k^2)^2 \ . \qquad (16)$$

The denominator expression in the correction term to $\overline{W}$ in Eq. (5) is the same for all operators since the auxiliary function ψ_{1T}^1 is independent of the particular operator whose expectation value is being determined. The expression is thus the same as derived in I. The solution of Eq. (9) is

$$f_i^1(r_i) = 1/4Z_1^3 r_i + r_i/2Z_1 - (1/2Z_1^2)\ln r_i + C_2 \ .$$

The orthogonalized auxiliary function ψ_{1T}^1 is

$$\psi_{1T}^1 = \left[\frac{1}{4Z_1^3}\left(\frac{1}{r_1} + \frac{1}{r_2} \right) - \frac{r_1 + r_2}{2Z_1} - \frac{1}{2Z_1^2}(\ln r_1 + \ln r_2) \right] \psi_{0T} + \frac{1}{Z_1^2}[\tfrac{5}{2} - \gamma - \ln 2Z_1]\psi_{0T} \ ,$$

where γ is the Euler's constant, $\gamma = 0.577\,215\,7$, and

$$1 + \int \psi_{1T}^1 (H - E) \psi_{0T} d\tau$$
$$= 1 + 3(Z_1 - Z)/Z_1 + (2/Z_1)(\tfrac{19}{32} - \tfrac{3}{8}\ln 2) \ . \qquad (17)$$

The determination of the numerator in the correction term to $\overline{W}$ is, however, not as straightforward because it is not possible to obtain the auxiliary function in simple analytic form. However, the principal point of interest is not so much to obtain ψ_{1T}^0 in some simple form, but rather to obtain a value for the integral $\int \psi_{1T}^0 (H - E)\psi_{0T} d\tau$. What we do, therefore, is to leave the function $f_i^0(r_i)$ in its integral form and substitute it directly into the numerator integral $\int \psi_{1T}^0 (H - E)\psi_{0T} d\tau$ and then solve for this quantity.

The analytic expression for the $f_i^0(r_i)$ ($i = 1, 2$ since the two electrons are equivalent) employed[7] in determining $\int \psi_{1T}^0 (H - E)\psi_{0T} d\tau$ is

$$f_i^0(r_i) = \left[\frac{4Z_1}{(4Z_1^2 + k^2)^2}\left(\frac{\cos kr_i}{r_i} - \cos k \right) + \frac{1}{4Z_1^3} + \frac{(4Z_1^2 - k^2)}{(4Z_1^2 + k^2)^2}\left(\frac{\sin kr_i}{kr_i} - \frac{\sin k}{k} \right) \right]$$
$$+ \left(\frac{4Z_1 k^2}{(4Z_1^2 + k^2)^2} \int_1^{r_i} \frac{\sin kr}{kr} dr - \frac{2Z_1}{(4Z_1^2 + k^2)} \int_0^{r_i} \frac{\sin kr}{kr} dr - \frac{8Z_1^2}{(4Z_1^2 + k^2)^2} \int_1^{r_i} \frac{\cos kr}{r} dr \right)$$

$$+\frac{16Z_1^4}{(4Z_1^2+k^2)^2}\left(\frac{r_i}{2Z_1}+\frac{\ln r_i}{2Z_1^2}-\frac{1}{4Z_1^3 r_i}\right)+C_1 \quad ,$$

where

$$C_1=\frac{1}{4Z_1^3}-\frac{4Z_1\cos k}{(4Z_1^2+k^2)^2}-\frac{(4Z_1^2-k^2)}{(4Z_1^2+k^2)^2}\,\frac{\sin k}{k}-\frac{4Z_1 k\,\mathrm{Si}(k)}{(4Z_1^2+k^2)^2}-\frac{2Z_1(4Z_1^2-k^2)}{k(4Z_1^2+k^2)^2}\tan^{-1}\frac{k}{2Z_1}-\frac{8Z_1^2(4Z_1^2-k^2)}{(4Z_1^2+k^2)^3}+\frac{16Z_1^2}{(4Z_1^2+k^2)^2}$$
$$-\frac{8Z_1^4}{(4Z_1^2+k^2)^2}\int_0^k\left(\frac{4}{k'(4Z_1^2+k'^2)}-\frac{1}{Z_1^2}\,\frac{\cos k'}{k'}\right)dk'$$

and where Si(k) is the sine integral defined by

$$\mathrm{Si}(k)=\int_0^k(\sin y/y)\,dy \quad .$$

The various components in the analytic expression for $\langle W\rangle\equiv F(k)$ are

$$\int\psi_{1T}^0(1/r_1)\psi_{0T}\,d\tau=\int\psi_{1T}^0(1/r_2)\psi_{0T}\,d\tau=-16Z_1^3k^2/A^3, \tag{18}$$

$$\int\psi_{1T}^0\frac{1}{r_{12}}\,\psi_{0T}\,d\tau=\frac{3Z_1^3}{A^2}\ln\frac{4A}{B}+\frac{3}{2}\,\frac{Z_1^2(4Z_1^2-k^2)}{kA^2}\left(\tan^{-1}\frac{k}{4Z_1}-\tan^{-1}\frac{k}{2Z_1}\right)-\frac{32Z_1^5(8Z_1^2-k^2)}{A^2B^2}$$
$$+\frac{4Z_1^3(4Z_1^2-k^2)}{A^2B}+\frac{6Z_1^3}{AB}+\frac{32Z_1^5}{AB^2}-\frac{96Z_1^5}{A^2B}-\frac{9}{2}\,\frac{Z_1^3}{A^2}+\frac{10Z_1^3(4Z_1^2-k^2)}{A^3} \quad ,$$

where

$$A=(4Z_1^2+k^2),\quad B=(16Z_1^2+k^2) \quad .$$

We note that the above analytic expression for the form factor is valid for *all* values of momentum transfer and for *all* elements of the isoelectronic sequence.

In Table I we compare our results for $F(k)\equiv\langle W\rangle$ for He I over the range of momentum transfer considered by Brown[5] together with those of (a) $\overline{W}$, employing the same ψ_{0T}, (b) $\langle W\rangle_0$, the form factor without the denominator expression in the correction term to $\overline{W}$ [see Eq. (5)] using the same trial wave function ψ_{0T}, i.e., of the first decoupling approximation,[2,8,9] (c) a three-term (six-parameter) analytic Hartree-Fock calculation due to Kim and Inokuti,[4] and (d) a 120-term configuration-interaction wave-function treatment due to Brown.[5]

We observe, first, that our results for $\langle W\rangle_0$ and $\langle W\rangle$ are equivalent to the analytic Hartree-Fock values of Kim and Inokuti. This is easily explained on the basis of Brillouin's theorem[10] according to which the expectation value of single-particle operators for closed-shell systems employing Hartree-Fock wave functions is correct to second order.[11] The expressions for both $\langle W\rangle_0$ and $\langle W\rangle$ are correct to second order[1,2] and thus lead to essentially equivalent results as those due to Hartree-Fock.

However, as the results due to Brown are considered to be correct to three significant figures, we wish to compare our results with his. We note that for low values of momentum transfer our results for $\langle W\rangle$ are correct to the third and, at times, to the fourth significant figure. The reason for such accuracy may be understood as follows: For low values of momentum transfer, the form factor $F(k)$ is given by the expansion[3,12]

$$F(k)\simeq Z-(k^2/3!)\langle r^2\rangle+O(k^4) \quad . \tag{19}$$

Thus for small k, the leading correction term is directly proportional to $\langle r^2\rangle$. As our technique gives[1] $\langle r^2\rangle$ to an accuracy of 99%, the correction term to Z is extremely small and hence our results for $F(k)$ for small k are excellent. In having substituted our value for $\langle r^2\rangle$ into the above equation we have inherently assumed (in order that our conclusions be self-consistent) that the expectation value of the operator r^2 as obtained via our technique is equivalent to the $\langle r^2\rangle$ obtained using the form factor. This assumption, however, is true as shown in Sec. III, where we prove a general theorem demonstrating the equivalence of the expectation value of any single-particle operator as obtained using our form factor to that of the expectation value determined using the technique directly.

On comparison of our results for $\langle W\rangle$ for small momentum transfer with those of $\langle W\rangle_0$ we note that our $\langle W\rangle$ values are superior. This of course is a consequence of the fact that the expectation value of r^2 as obtained by Shustek and Krieger[8] employing a technique similar to ours but using the analytic expression for the expectation value as obtained in the first decoupling approximation[2] is in error by 2.7%. (The equivalence theorem mentioned above and discussed in Sec. III holds for their technique as well.)

The maximum error in our results of approximately 1% occurs for certain values in the median range of momentum transfer considered in Table I and diminishes again for larger values of k. For example, at a momentum transfer of 1 Å^{-1}, the error in $\langle W\rangle$ is 0.9%. However, the improvement over $\overline{W}$ is quite striking since at the above value of momentum transfer $\overline{W}$ is in error by 13%. At a momentum transfer of 2 Å^{-1} a 24% error in $\overline{W}$ is reduced to a 0.85% error in $\langle W\rangle$.

Except for a small range of momentum transfer between 0.35 and 0.55 Å^{-1}, our results for $\langle W\rangle$ are superior to those of $\langle W\rangle_0$ over the entire medium- and high-momentum-transfer ranges considered. At the momentum transfer of 1 Å^{-1}, $\langle W\rangle_0$ is in error by 1.3% and at 2 Å^{-1} the error in $\langle W\rangle_0$ is 3.1%. This behavior of $\langle W\rangle_0$ for the helium atom, of increasing error with increasing momentum transfer, is entirely similar to its behavior for the hydrogen atom as discussed in the preceding paper[2] where it diverged further from the exact result the greater the momentum transfer. $\langle W\rangle$ on the other hand tends to converge to nearly the correct answer for large values of momentum transfer for both the hydrogen and helium atoms.

Here again as in the case of the results of I for the expectation values of other single-particle operators, we expect our results for the form factor to improve for each heavier element of the isoelectronic sequence as the interelectronic potential term in the Hamiltonian becomes less and less significant in comparison to the electron-nuclear potential terms, thereby making correlation terms which are neglected here less significant. On comparison of our results for $\langle W\rangle$ with those of Brown,[5] this is found to be the case. Similar results obtain for Li II.[5,7] Here, for low values of k our results are the same as his to four and, at times, to five significant figures. In the median range again there is a maximum error of approximately 0.4% and for the largest value of momentum transfer considered by Brown (3.0555 Å^{-1}) a 16% error in $\overline{W}$ is reduced to a 0.25% error in $\langle W\rangle$. Our results for the remaining elements of the isoelectronic sequence improve for each heavier element.[5,7]

Womack and Nickerson[13] have also performed an approximate analytic calculation of the form factor for the helium isoelectronic sequence using large-Z perturbation theory through order Z^{-1}. We find their calculation accounts for less than half of the difference between our lowest-order term $\overline{W}$ and the results due to Brown for He, and is in error by approximately 10% for a momentum transfer of 1 Å^{-1}, the largest value tabulated by them. For larger values of Z, the accuracy of their results improves as expected, but are not generally substantially better than $\overline{W}$ alone.

III. EXPECTATIONS OF SINGLE-PARTICLE OPERATORS FROM COHERENT ATOMIC SCATTERING FACTOR $F(k)$

As the form factor $F(k)$ is the Fourier transform of the electron density, the electron density is given by

$$\rho(r) = (1/8\pi^3)\int F(k)\, e^{-i\vec{k}\cdot\vec{r}}\, d\vec{k} \quad . \tag{20}$$

The expectation value of an arbitrary single-particle operator W which is a function of the radial distance in terms of the electron density is

$$\langle W\rangle = \int W\rho(r)\, d\vec{r} \tag{21}$$

so that on substituting for $\rho(r)$ from (20) into (21) we have

$$\langle W\rangle = \int W(r)[(1/8\pi^3)\int F(k)\, e^{-i\vec{k}\cdot\vec{r}}\, d\vec{k}]\, d\vec{r} \quad . \tag{22}$$

Thus knowledge of the form factor permits the determination of the expectation value of any such operator W. Now the technique discussed in I and the preceding paper[2] is essentially a method for the determination of the expectation values of single-particle operators $W=\sum_i W(r_i)$. What we wish to prove here is that the expectation value of any arbitrary single-particle operator W as determined via this technique is entirely equivalent to the expectation value of the operator as given in terms of the form factor $F(k)$ by Eq. (22), where the form factor itself has been obtained via our method as the expectation value of the operator $V=\sum_i[(\sin kr_i)/kr_i]$ with the same choice for ψ_{0T}. Thus we seek to show that

$$\langle W\rangle = \overline{W} + \frac{2\,\mathrm{Re}\int \psi^{0*}_{1T(W)}(H-E)\psi_{0T}\, d\tau}{1+\mathrm{Re}\int \psi^{1*}_{1T}(H-E)\psi_{0T}\, d\tau}$$

$$= \int W(r)[(1/8\pi^3)\int \langle V\rangle\, e^{-i\vec{k}\cdot\vec{r}}\, d\vec{k}]\, d\vec{r} \quad , \tag{23}$$

where $\psi^0_{1T(W)}$ in the above expression is the auxiliary function ψ^0_{1T} which may be obtained by direct use of the analytical method involving the specific operator W in question and where $\langle V\rangle \equiv F(k)$. The auxiliary function for the operator V is similarly designated $\psi^0_{1T(V)}$.

Since we ensure the orthogonality of the auxiliary functions $\psi^0_{1T(W)}$, $\psi^0_{1T(V)}$, and ψ^1_{1T} to ψ_{0T} we may replace the generally unknown energy E in Eq. (23) by any suitable quantity. If we replace it by the expectation value of the Hamiltonian in the state ψ_{0T}, i.e., by $\mathcal{E}=\langle\psi_{0T}|H|\psi_{0T}\rangle$, then the addition of any orthogonality terms to the unorthogonalized auxiliary functions $\psi^0_{1T(W)}$, $\psi^0_{1T(V)}$, and ψ^1_{1T} leads to no net contribution to the integrals in the correction terms to $\overline{W}$ and $\overline{V}$. This implies therefore that if we substitute $\mathcal{E}$ for the energy E then these integrals are independent of the constants required to orthogonalize the auxiliary functions to

TABLE I. Comparison of form factors $F(k)$ for He I. Here

$$\overline{W}=\int\psi_{0T}^{*}\,W\psi_{0T}\,d\tau,\qquad \langle W\rangle_0=\overline{W}+2\,\mathrm{Re}\int\psi_{1T}^{0*}\,(H-E)\,\psi_{0T}\,d\tau,$$

$$\langle W\rangle=\overline{W}+\left[2\mathrm{Re}\int\psi_{1T}^{0*}\,(H-E)\,\psi_{0T}\,d\tau/\left(1+\mathrm{Re}\int\psi_{1T}^{1*}\,(H-E)\,\psi_{0T}\,d\tau\right)\right].$$

$(\sin\frac{1}{2}\theta)/\lambda$ (Å^{-1})	ka_0	$\overline{W}$	$\langle W\rangle_0$	$\langle W\rangle$	AHF[a]	CI[b]
0.0	0.0	2.0000	2.0000	2.0000	2.0000	2.0000
0.025	0.166243	1.9903	1.9894	1.9892	1.9892	1.9891
0.050	0.332485	1.9617	1.9579	1.9572	1.9571	1.9569
0.075	0.498728	1.9154	1.9073	1.9058	1.9057	1.9052
0.100	0.664971	1.8533	1.8399	1.8373	1.8372	1.8364
0.150	0.997456	1.6916	1.6668	1.6621	1.6626	1.6612
0.200	1.32994	1.4985	1.4650	1.4587	1.4604	1.4585
0.250	1.66243	1.2952	1.2579	1.2508		1.2522
0.300	1.99491	1.0984	1.0625	1.0557	1.0602	1.0586
0.350	2.32740	0.91859	0.88813	0.88233		0.88626
0.400	2.65988	0.76102	0.73812	0.73376	0.7383	0.73794
0.450	2.99237	0.62692	0.61210	0.60928		0.61313
0.500	3.32485	0.51508	0.50775	0.50636	0.5089	0.50953
0.550	3.65734	0.42305	0.42201	0.42181		0.42420
0.600	3.98981	0.34794	0.35181	0.35255	0.3529	0.35416
0.650	4.32231	0.28693	0.29436	0.29577		0.29671
0.700	4.65480	0.23745	0.24727	0.24914	0.2481	0.24952
0.750	4.98728	0.19733	0.20859	0.21074		0.21067
0.800	5.31977	0.16472	0.17671	0.17899	0.1772	0.17860
0.850	5.65225	0.13816	0.15034	0.15266		0.15203
0.900	5.98474	0.11645	0.12844	0.13073	0.1288	0.12995
0.950	6.31722	0.098611	0.11019	0.11239		0.11154
1.00	6.64971	0.083913	0.094905	0.096997	0.09523	0.096123
1.05	6.98219	0.071742	0.082062	0.084026		0.083167
1.10	7.31468	0.061617	0.071227	0.073054	0.07152	0.072239
1.15	7.64717	0.053155	0.062046	0.063739		0.062983
1.20	7.97965	0.046052	0.054242	0.055801	0.05453	0.055114
1.25	8.31214	0.040061	0.047582	0.049014		0.048398
1.30	8.64462	0.034988	0.041878	0.043189	0.04216	0.042643
1.35	8.97711	0.030672	0.036976	0.038176		0.037695
1.40	9.30959	0.026987	0.032747	0.033844	0.03302	0.033424
1.45	9.64208	0.023826	0.029088	0.030090		0.029725
1.50	9.97456	0.021106	0.025912	0.026827	0.02617	0.026511
1.60	10.6395	0.016717	0.020730	0.021494		0.021257
1.70	11.3045	0.013395	0.016754	0.017395		0.017216
1.80	11.9695	0.010849	0.013669	0.014206		0.014071
1.90	12.6344	0.0088723	0.011250	0.011703		0.011599
2.00	13.2994	0.0073213	0.0093351	0.0097185		0.0096363

[a] Column AHF refers to the analytic Hartree-Fock calculations due to Kim and Inokuti (see Ref. 4).

[b] Column CI refers to the 120-term configuration-interaction result due to Brown (see Ref. 5).

ψ_{0T}. In proving the above theorem we may thus only consider the unorthoganalized auxiliary functions. In addition, since the operators W and V are sums of single-particle operators, it is sufficient to prove the theorem for a single term $f_i^0\psi_{0T}$ of the auxiliary function ψ_{1T}^0. (The subscript i is thus dropped.)

Let us first consider $\overline{V}=\langle\psi_{0T}\,|\,(\sin kr)\,|\,kr\,|\,\psi_{0T}\rangle$ of $\langle V\rangle$. As a consequence of the Fourier integral theorem it may be seen that

$$\overline{W}=\int W(r)\left[(1/8\pi^3)\int\overline{V}e^{-i\vec{k}\cdot\vec{r}}d\vec{k}\right]d\vec{r}\quad . \tag{24}$$

The denominator expression in the correction terms to $\overline{W}$ and $\overline{V}$ of both $\langle W\rangle$ and $\langle V\rangle$ is the same and is independent of $\vec{k}$ since the auxiliary function ψ_{1T}^1 is independent of the operator in question. Thus we next have to consider the numerator integral in the correction term to $\overline{V}$. For this term of $\langle V\rangle$ in Eq. (22) we have (here $d\tau'$ refers to integrals over the configuration space of all the electrons in the system)

$$\int W(r)\{(1/8\pi^3)\int[\int \psi^{0*}_{1T(V)}(H-\mathcal{E})\psi_{0T}\,d\tau']\times e^{-i\vec{k}\cdot\vec{r}}\,d\vec{k}\}\,d\vec{r}\ ,$$

$$\psi^0_{1T(V)}=f^0_V(r)\psi_{0T}\ , \tag{25}$$

where $f^0_V(r)$ is the $f^0(r)$ function taken with respect to the operator $V=(\sin kr)/kr$ and $\psi^0_{1T(V)}$ the corresponding auxiliary function. Now the function $f^0_V(r)$ as given by Eq. (10) is a sum of two terms. Let us consider the first term, i.e., the part of $f^0_V(r)$ defined as

$$\xi^0_V(r)=\int_a^r \frac{1}{r'^2\phi^2(r')}\times\left(\int_\infty^{r'}\phi^2(r'')\frac{\sin kr''}{kr''}\,r''^2\,dr''\right)dr'\ , \tag{26}$$

where a is some arbitrary lower limit. For this part of $f^0_V(r)$ the integral in Eq. (25) is

$$\int W(r)\left(\frac{1}{2\pi^2}\cdot\int_0^\infty\left\{\int\left[\int_a^{r'}\frac{1}{r''^2\phi^2(r'')}\left(\int_\infty^{r''}\phi^2(r''')[(\sin kr''')/kr''']r'''^2\,dr'''\right)dr''\right]\times\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau'\right\}\frac{\sin kr}{kr}\,k^2dk\right)d\vec{r}\ . \tag{27}$$

By consistent and repeated changes in the order of integration we may reduce the previous integral to

$$\frac{2}{\pi}\int\left(\int_a^{r'}\frac{1}{r''^2\phi^2(r'')}\left\{\int_\infty^{r''}\phi^2(r''')r'''^2\left[\int_0^\infty W(r)\left(\int_0^\infty\frac{\sin kr}{kr}\,\frac{\sin kr'''}{kr'''}\,k^2\,dk\right)r^2dr\right]dr'''\right\}dr''\right)\times\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau'\ . \tag{28}$$

Now it may be shown using distribution theory[14] that for physically realizable systems

$$\int_0^\infty \sin kr'\,\sin kr\,dk=\tfrac{1}{2}\pi\,\delta(r'-r)\ ,$$

so that on substitution of this integral, expression (28) reduces to

$$\int\left[\int_a^{r'}\frac{1}{r''^2\phi^2(r'')}\left(\int_\infty^{r''}\phi^2(r''')W(r''')r'''^2\,dr'''\right)dr''\right]\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau'\ , \tag{29}$$

where the integral from a to r' within the square brackets may be recognized immediately as $\xi^0_W(r)$, the first part of $f^0(r)$ derived for the operator $W(r)$, i.e., expression (29) is simply

$$\int \xi^0_W(r)\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau'\ . \tag{30}$$

The second part $\zeta^0_V(r)$ of $f^0_V(r)$ defined as

$$\zeta^0_V(r)=\int_a^r\frac{1}{r'^2\phi^2(r')}\left(\int_\infty^{r'}\phi^2(r'')\,\bar{V}\,r''^2\,dr''\right)dr'$$

may be treated in exactly the same manner to prove that

$$\int W(r)\{(1/8\pi^3)\int[\int \zeta^0_V\,\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau']e^{-i\vec{k}\cdot\vec{r}}\,d\vec{k}\}\,d\vec{r}$$

$$=\int \zeta^0_W\,\psi^*_{0T}(H-\mathcal{E})\psi_{0T}\,d\tau'\ . \tag{31}$$

Therefore Eq. (23) holds and the theorem regarding the equivalence of the two techniques for obtaining $\langle W\rangle$ is thus proved.

The statements of the previous few paragraphs are general in that they apply to any operator of the form $W=\sum_i W(r_i)$. Moreover, we give below specific analytic expressions for the operators considered in I, namely, $r^n, n=2, 1, -1, -2$, and the electron density at the origin in terms of the coherent form factor $F(k)$ employing Eq. (22)[15,7]:

$$\langle r^2\rangle=-\nabla_k{}^2F(k)\big|_{k=0}\ , \tag{32a}$$

$$\langle r\rangle=(2/\pi)\int_0^\infty -\nabla_k{}^2F(k)\,dk\ , \tag{32b}$$

$$\langle r^{-1}\rangle=(2/\pi)\int_0^\infty F(k)\,dk\ , \tag{32c}$$

$$\langle r^{-2}\rangle=\int_0^\infty kF(k)\,dk\ , \tag{32d}$$

$$\langle\delta(\vec{r})\rangle=(1/2\pi^2)\int_0^\infty k^2F(k)\,dk\ . \tag{32e}$$

We may thus employ the analytic expression for $F(k)$ derived in Sec. II to rederive our results of I via the above formulas; i.e., it is no longer necessary to calculate the expectation value correct to second order of each single-particle operator separately since they can all be obtained from the Fourier transform of the charge density calculated correct to second order.

These analytic expressions also enable us to understand better some of the results obtained in I. There, for example, for the ground state of the helium atom we had overestimated the results for $\langle r^{-2}\rangle$ and $\langle\delta(\vec{r})\rangle$ on comparison with those due to Pekeris.[16] This may be explained on the basis of the fact [see Eqs. (32d) and (32e)] that to obtain the expectation values $\langle r^{-2}\rangle$ and $\langle\delta(\vec{r})\rangle$ we need to integrate the form factor weighted for large k over an infinite range of momentum transfer. Note that our results for $F(k)\equiv\langle W\rangle$ lie slightly above those due to Brown for values of momentum transfer above 0.75 Å^{-1} and hence on integrating over all values of k we arrive at an overestimate for the expectation values of these operators.

Finally having derived an analytical expression for the coherent scattering form factor valid for all values of momentum transfer we are able to extend our calculations to the infinite-momentum-transfer limit. However, results for $F(k)$ due to Brown and Kim and Inokuti for values of momentum transfer greater than those considered in Table I are unavailable and thus we can no longer compare our results with theirs. We may, however, study our results for the infinite-momentum-transfer limit by employing a cusp condition due to Kato[6] describing the behavior of the exact ground-state wave function of a two-electron system in the limit of coalescence of one electron with the nucleus.

TABLE II. $F(k)$ for large momentum transfer. Comparison of coefficients of terms of order k^{-4}.

Z	Pekeris[a] + cusp condition	Present work	% error
1	16.5373	17.1174	3.5
2	364.003	366.091	0.57
3	2066.48	2071.45	0.24
4	6915.73	6924.87	0.13
5	17 471.4	17 486.2	0.09
6	37 061.6	37 083.2	0.06
7	69 781.9	69 811.7	0.04
8	120 495.6	120 535.4	0.03

[a] See Ref. 16.

This follows from the fact that[17]

$$F(k)_{k\to\infty}=\left(-8\pi\frac{d\rho}{dr}\bigg|_{r=0}\right)\frac{1}{k^4} \tag{33}$$

and since the cusp condition may be written as[6]

$$\frac{d\rho}{dr}\bigg|_{r=0}=-2Z\rho(0)\ , \tag{34}$$

Goscinski and Lindner, using Eqs. (33) and (34), obtained the asymptotic expression for the form factor:

$$F(k)_{k\to\infty}=16Z\pi\rho(0)\frac{1}{k^4}\ . \tag{35}$$

Expanding our analytic expression for $F(k)$ in the $k\to\infty$ limit we obtain

$$F(k)_{k\to\infty}=\left(32Z_1^4-\frac{Z_1^3[128(Z_1-Z)+38-12\ln 4]}{1+3(Z_1-Z)/Z_1+(2/Z_1)(\frac{19}{32}-\frac{3}{8}\ln 2)}\right)\frac{1}{k^4}\ . \tag{36}$$

We may thus compare our results for the form factor in the infinite-momentum-transfer limit as given by Eq. (36) with those of an "exact" calculation by substituting into Eq. (35) the most accurate value of $\rho(0)$ available, namely, those due to Pekeris.[16] In Table II we compare the coefficients of k^{-4} with those involving the results of Pekeris for $\rho(0)$. We observe that the error for He is 0.57% and that this error again decreases for each heavier element of the isoelectronic sequence as expected. The form factor in the infinite-momentum-transfer limit for the negative ion of atomic hydrogen H$^-$, whose properties we know are highly sensitive to the choice of the wave function employed,[18] however, differs by only 3.5% from an "exact" calculation, whereas $\bar{W}$ in this case is in error by 57.8%. Benesch and Smith,[19] employing a 20-parameter Hylleraas-type wave function not satisfying the Kato cusp condition, have also calculated the coefficient of k^{-4} in the high k limit. For $Z=1, 2, 3$ their results, compared to those of Pekeris listed in column one of Table II, are in error by 1.5%, 0.21%, 0.20% and are thus more accurate than ours. However, for $Z\geq 5$ our results are slightly more accurate than theirs.

We note also that the cusp condition, as written in terms of the relationship between the logarithmic derivative of the electron density at the origin and the atomic number, Eq. (34), is exactly satisfied on substitution of our analytic expressions for the expectation value of the electron density at the origin from I which is (here the first term corresponds to W and the second to the correction to $\bar{W}$ in the second decoupling approximation)

$$\rho(0)=\frac{2Z_1^3}{\pi}-\frac{\pi^{-1}[6Z_1^2(Z_1-Z)+4\gamma Z_1^2]}{1+3(Z_1-Z)/Z_1+(2/Z_1)(\frac{19}{32}-\frac{3}{8}\ln 2)}$$

$$=-\frac{1}{2Z}\frac{d\rho}{dr}\bigg|_{r=0}\ , \tag{37}$$

with $\gamma=\frac{19}{32}-\frac{3}{8}\ln 2$ and where the radial derivative is obtained from Eqs. (33) and (36). In addition, the satisfaction of this cusp condition is observed to be independent of the choice of the variational parameter Z_1.

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[‡] On leave of absence from the Polytechnic Institute of Brooklyn, Brooklyn, New York.

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X-Ray Scattering from Liquid Crystals. I. Cholesteryl Nonanoate and Myristate

W. L. McMillan
Bell Laboratories, Murray Hill, New Jersey 07974

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X-ray scattering intensities from unoriented samples of cholesteryl nonanoate and myristate are reported for several temperatures in the smectic *A*, cholesteric, and isotropic liquid phases. The measured Bragg-scattering intensities from the smectic planes are used to test a recent theoretical model of the smectic *A* phase. Strong pretransition scattering (short-range-order or order-parameter fluctuations) are observed in the cholesteric phase and a Landau theory is constructed to describe this effect.

I. INTRODUCTION

In his classic study of liquid crystals Friedel[1] differentiated three types of phases—nematic, cholesteric, and smectic. The nematics and cholesterics exhibit orientational order with the long molecular axis oriented preferentially parallel to an axis in space. In cholesterics this preferred axis has a helical twist but from the thermodynamic point of view the two phases are the same. The nematic is just a cholesteric with infinite helical pitch. For the smectics then under study Friedel[1] postulated and Friedel[2] verified a planar structure.

The nematics and cholesterics have been studied intensively for the last few years and the theoretical situation is well advanced. One has a microscopic theory due to Maier and Saupe,[3] a continuum elastic theory[4,5] which has been extended