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Large-momentum-transfer limit of some matrix elements

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The matrix element $\epsilon_{fi}(K)$, or ϵ, that appears in the study of elastic and inelastic electron-atom scattering from an initial state i to a final state f in the first Born approximation depends explicitly on the momentum transfer $\hbar\vec{K}$. The uncertainty in the value of the calculated cross sections arises not only from the application of the Born approximation but also from the approximate nature of the wave functions used. For the $1\,^1S$-$2\,^1P$ transition in helium, we present an analytic expression in terms of the $1\,^1S$ and $2\,^1P$ wave functions for the leading coefficient C_1 in the asymptotic expansion of ϵ as a power series in $1/K$; C_1 is defined by $\epsilon \sim C_1/K^5$ as $K \sim \infty$. An accurate numerical value of C_1 is obtained by using a sequence of better and better $1\,^1S$ and $2\,^1P$ wave functions. An accurate value of C_1 can be useful in obtaining an approximate analytic form for the matrix element. We also present analytic expressions, in terms of the $1\,^1S$ wave function, for the coefficients of the two leading terms of ϵ for the diagonal case, that is, for the atomic form factor, and we obtain accurate estimates of those coefficients. The procedure is easily generalizable to other matrix elements of helium, but it would be difficult in practice to apply the procedure to matrix elements of other atoms. We also give a very simple approximate result, valid for a number of matrix elements of heavy atoms, for the ratios of the coefficients of successive terms (in the asymptotically high-K domain) in a power series in $1/K$. Finally, we plot ϵ for $1\,^1S$ to $1\,^1S$ and for $1\,^1S$ to $2\,^1P$, with the known low-K and high-K dependence extracted. One might hope that each plot would show little variation, but the $1\,^1S$ to $1\,^1S$ plot varies considerably as one goes to high K, and the $1\,^1S$ to $2\,^1P$ plot shows a very rapid variation for $K \sim \infty$, strongly suggesting that at least one element of "physics"—perhaps a pole outside of but close to the domain of convergence—has been omitted.

I. INTRODUCTION

In studying the elastic or inelastic collisions of an electron with an atom, it is often sufficiently accurate and convenient, when the incident electron has sufficiently high energy, to use the first Born approximation. The matrix elements that appear in calculating cross sections in the first Born approximation are found to be of the form[1]

$$\epsilon_{fi}(K) = \int \phi_f^* \sum_j \exp(i\vec{K}\cdot\vec{r}_j)\phi_i d\vec{r}, \tag{1.1}$$

where $\hbar\vec{K}$ is the momentum transfer, $\vec{r}_j$ is the position of the jth electron, and ϕ_i and ϕ_f are the normalized initial- and final-state wave functions. We will sometimes write ϵ for $\epsilon_{fi}(K)$. The integration is performed over the coordinates of all the target electrons; the coordinate of the incident electron does not appear. The diagonal and off-diagonal matrix elements are related to the atomic form factor and the generalized oscillator strengths, respectively.[2] When the target is an atom other than hydrogen, there is, in addition to the uncertainty due to the application of the Born approximation, an uncertainty arising from the necessarily approximate nature of the wave functions used. These considerations have aroused a great deal of interest[3] in the possibility of obtaining analytic expressions for the form factors and for generalized oscillator strengths, or even a "reasonably accurate" approximate analytic form. (Recent developments in dispersion theory,[4] in connection with electron-hydrogen atom scattering, in which new singularities in the full Green's functions have apparently been revealed, should give more information on the nature of wave functions. This suggests that now might be a good time to attempt to develop such analytic forms, but we shall not here make such an attempt. See, however, Sec. IV.) As one application the open parameters could be chosen to fit the experimental data in the experimentally accessible domains (or domains where data are available) and could then be used to predict values in experimentally inaccessible domains (or domains where data are not available). As a second application the theoretical evaluation of ϵ, for a given choice of $\hbar\vec{K}$ and of ϕ_i and ϕ_f, can be very time consuming, and it would therefore also be useful to have an analytic form for ϵ which could be matched to theoretical estimates for a few values of $\hbar\vec{K}$, and then used to estimate values of ϵ for other values of $\hbar\vec{K}$. Matrix elements of the form (1.1) also appear in the cross section for the photoeffect for electrons emitted with sufficiently high energy.[5]

We will begin by considering the asymptotic behavior of ϵ, defined by (1.1), which will behave as $(Ka_0)^{-n}$, with n known, with corrections of higher order in $1/K$. If a useful analytic form for ϵ were available, an accurate value of the coefficient of

$(Ka_0)^{-n}$ would be very helpful in fixing the constants. Furthermore, we will consider only a few transitions for the particular case of helium. It has been shown[6] using simply the selection rules implied in the angular integral of ϵ that the leading term in the asymptotic expansion ($K\sim\infty$) of ϵ is given by

$$\epsilon \sim \text{const}(Ka_0)^{-(l_i+l_f+4)}, \tag{1.2}$$

where l_i and l_f are the angular-momentum quantum numbers of the active electron's orbitals of the initial and final states, respectively. However, few numerical estimates have been obtained previously for any of the coefficients of the leading terms in these asymptotic expansions. We will estimate the coefficient (or the two leading coefficients) numerically and will give the forms for the next few coefficients, for certain transitions in helium, valid for any choice of wave functions. The procedure, even though illustrated here only for helium, can be easily generalized to other atoms.

We note that large momentum transfers occur at small impact parameters so that the region of configuration space that is of relevance in the asymptotic behavior of ϵ is the region close to the nucleus; for large momentum transfer, the exponential factor in Eq. (1.1) for ϵ oscillates very rapidly so that the main contribution to the matrix element comes from small values of the associated r, from zero to of the order of $1/K$. This is also the region of configuration space that is relevant in the calculation of hyperfine interactions and of isotope shifts. In fact, the leading coefficient in the asymptotic expansion of the atomic form factor can be related to the volume isotope shift via sum rules.[7]

Finally, we will be using, for some simplifications, the cusp conditions of Kato. These cusp conditions arise due to the electron-electron and electron-nucleus Coulomb singularities of the Schrödinger equation (neglecting spin interactions). Kato[8] showed that at these singularities the following cusp conditions in the n-electron wave function $\phi(\vec{r}_1,\ldots,\vec{r}_n)$ hold.

(a) the singularity arising from $r_i=0$ $(i=1,\ldots,n)$:

$$\left.\frac{\partial\bar{\phi}}{\partial r_i}\right|_{r_i=0} = -Z\phi(\vec{r}_1,\ldots,\vec{r}_{i-1},0,\vec{r}_{i+1},\ldots,\vec{r}_n)/a_0, \tag{1.3}$$

where $\bar{\phi}$ is obtained by averaging ϕ over the surface of the sphere $r_i=$ constant, keeping the positions of the other $(n-1)$ electrons fixed on both sides of Eq. (1.3).

(b) the singularity arising from $r_{ij}=0$ $(i,j=1,\ldots,n)$:

$$\left.\frac{\partial\bar{\phi}}{\partial r_{ij}}\right|_{r_{ij}=0} = +\tfrac{1}{2}\phi(\ldots,\vec{r}_{i-1},\vec{r},\vec{r}_{i+1},\ldots,\vec{r}_{j-1},\vec{r},\vec{r}_{j+1},\ldots)/a_0, \tag{1.4}$$

where $\bar{\phi}$ now is obtained from ϕ by rotating $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$ over the surface of the sphere $r_{ij}=$ constant, keeping $\vec{r}=\frac{1}{2}(\vec{r}_i+\vec{r}_j)$ and the other $(n-2)$ position vectors (all except the ith and jth electron positions) fixed on both sides of Eq. (1.4).

The cusp conditions quoted above are rigorous conditions applicable at points at which two particles coincide. Singularities also arise when more than two particles coincide. These singularities are presumably less significant than the two-particle singularities, and we will not concern ourselves with such singularities. The nature of the singularity when both electrons, in a two-electron atom, simultaneously come close to the nucleus is known—it leads to logarithmic terms in the two-electron wave function.[9]

II. LARGE-MOMENTUM-TRANSFER LIMIT

A. Diagonal matrix element

The atomic form factor $F(K)$ for a neutral atom of atomic number Z is defined by

$$F(K)\equiv\epsilon_{11}(K)=\left\langle\phi_1\left|\sum_{j=1}^{Z}\exp(i\vec{K}\cdot\vec{r}_j)\right|\phi_1\right\rangle, \tag{2.1}$$

where ϕ_1 is the ground-state wave function of the atom. As noted above, $F(K)$ appears in the elastic scattering of electrons from an atom, in the first Born approximation.

We will now consider the asymptotic behavior of $\epsilon_{11}(K)$ for helium ($Z=2$). The ground-state wave function of helium depends only on r_1, r_2, and r_{12}, the three sides of the triangle formed by the nucleus and the two electrons, that is, $\phi_1=\phi_1(r_1,r_2,r_{12})$. We then have

$$\begin{aligned}\epsilon_{11}(K)&=\langle\phi_1|\exp(i\vec{K}\cdot\vec{r}_1)+\exp(i\vec{K}\cdot\vec{r}_2)|\phi_1\rangle\\&=2\langle\phi_1|j_0(Kr_1)|\phi_1\rangle,\end{aligned} \tag{2.2}$$

where we have used the symmetry of ϕ_1 under the interchange of $\vec{r}_1$ and $\vec{r}_2$, have expanded the plane wave into partial waves, and have used the fact that ϕ_1 has total orbital angular momentum $L=0$. $\epsilon_{11}(K)$ can be further rewritten formally as the one-dimensional integral

$$\epsilon_{11}(K)=2\int_0^\infty r_1^2dr_1\,j_0(Kr_1)A(r_1), \tag{2.3a}$$

where, with $d\Omega_1=\sin\theta_1\,d\theta_1\,d\varphi_1$,

$$A(r_1)\equiv\int d\Omega_1\int d\vec{r}_2\phi_1^*\phi_1 \tag{2.3b}$$

is independent of the momentum transfer $\hbar\vec{K}$ and does not vanish at $r_1 = 0$. $A(r_1)$ is related to the angular average of the first-order density matrix. Making use of the boundary condition on $A(r_1)$, namely, that it vanish at infinity, and writing $j_0(Kr_1) = \sin(Kr_1)/Kr_1$, Eq. (2.3a) can be integrated by parts successively to get the asymptotic expansion

$$\epsilon_{11}(K) = -\frac{4}{K^4}\sum_{n=0}^{\infty}\frac{(-1)^n(n+1)}{K^{2n}}\frac{d^{2n+1}A(r_1)}{dr_1^{2n+1}}\bigg|_{r_1=0}. \tag{2.4}$$

The leading term in the asymptotic expansion (2.4) has, of course, the K dependence predicted by Rau and Fano[6]; see Eq. (1.2). The region of configuration space that is of relevance is the region close to the nucleus.

To obtain explicit expressions for the coefficients of the first few terms in the expansion (2.4), in terms of ϕ_1, we need derivatives of the function $A(r_1)$ defined by (2.3b). For $r_1 \sim 0$, we can expand r_{12} as

$$r_{12} = r_2 - \mu r_1 + [(1-\mu^2)/2r_2]r_1^2 + [\mu(1-\mu^2)/2r_2^2]r_1^3 + O(r_1^4), \tag{2.5}$$

where $\mu = \hat{r}_1 \cdot \hat{r}_2$. Using (2.5), an *arbitrary* function $g(r_1, r_2, r_{12})$ can be expanded as a power series in r_1 by expanding about $r_1 = 0$ and $r_{12} = r_2$. We find

$$\begin{aligned} g(r_1, r_2, r_{12}) = {} & g(0, r_2, r_2) + (g_1 - \mu g_{12})r_1 + [\tfrac{1}{2}(1-\mu^2)g_{12}/r_2 + \tfrac{1}{2}g_{1,1} - \mu g_{1,12} + \tfrac{1}{2}\mu^2 g_{12,12}]r_1^2 \\ & + [\tfrac{1}{2}\mu(1-\mu^2)g_{12}/r_2^2 + \tfrac{1}{2}(1-\mu^2)g_{1,12}/r_2 - \tfrac{1}{2}\mu(1-\mu^2)g_{12,12}/r_2 \\ & + \tfrac{1}{6}g_{1,1,1} - \tfrac{1}{2}\mu g_{1,1,12} + \tfrac{1}{2}\mu^2 g_{1,12,12} - \tfrac{1}{6}\mu^3 g_{12,12,12}]r_1^3 + O(r_1^4), \end{aligned}$$

where

$$g_1 \equiv \frac{\partial g}{\partial r_1}\bigg|_{r_1=0}, \quad g_{12} \equiv \frac{\partial g}{\partial r_{12}}\bigg|_{r_1=0}, \quad g_{1,12} \equiv \frac{\partial^2 g}{\partial r_1 \partial r_{12}}\bigg|_{r_1=0}, \ldots. \tag{2.6}$$

Making this kind of expansion for the integrand in (2.3b), we have

$$\begin{aligned} A(r_1) &= 8\pi^2\int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12}\frac{1}{r_1}\phi_1^*\phi_1 \\ &= 8\pi^2\int_0^\infty r_2 dr_2\Bigg\{2r_2|\phi_1(0,r_2,r_2)|^2 + 2r_1 r_2\left(\frac{\partial(\phi_1^*\phi_1)}{\partial r_1}\bigg|_{r_1=0}\right) + \frac{1}{3}r_1^2\left[\left(2\frac{\partial}{\partial r_{12}} + 3r_2\frac{\partial^2}{\partial r_1^2} + r_2\frac{\partial^2}{\partial r_{12}^2}\right)\phi_1^*\phi_1\bigg|_{r_1=0}\right] \\ &\quad + \frac{1}{3}r_1^3\left[\left(2\frac{\partial^2}{\partial r_1\partial r_{12}} + r_2\frac{\partial^3}{\partial r_1^3} + r_2\frac{\partial^3}{\partial r_1\partial r_{12}^2}\right)\phi_1^*\phi_1\bigg|_{r_1=0}\right] + O(r_1^4)\Bigg\}. \end{aligned} \tag{2.7}$$

The asymptotic expansion (2.4) can be rewritten as

$$\epsilon_{11}(K) = I/(Ka_0)^4 + J/(Ka_0)^6 + O(1/(Ka_0)^8), \tag{2.8}$$

where the coefficients of the leading terms are

$$I = -64\pi^2 a_0^4\int_0^\infty r_2^2 dr_2\frac{\partial(\phi_1^*\phi_1)}{\partial r_1}\bigg|_{r_1=0}, \tag{2.9a}$$

and

$$J = 128\pi^2 a_0^6\int_0^\infty r_2^2 dr_2\left(\frac{2}{r_2}\frac{\partial^2}{\partial r_1\partial r_{12}} + \frac{\partial^3}{\partial r_1^3} + \frac{\partial^3}{\partial r_1\partial r_{12}^2}\right)\phi_1^*\phi_1\bigg|_{r_1=0}. \tag{2.10}$$

Using the Kato cusp condition (1.3), we can rewrite I as

$$I = 256\pi^2 a_0^3\int_0^\infty r_2^2 dr_2(\phi_1^*\phi_1)\bigg|_{r_1=0}. \tag{2.9b}$$

For later purposes, it will also be useful to write this in the form

$$I = 64\pi a_0^3\int d\vec{r}_1 d\vec{r}_2\phi_1^*\phi_1\delta(\vec{r}_1). \tag{2.9c}$$

We can immediately generalize this result from helium to the isoelectronic sequence associated with helium; we need merely multiply Eqs. (2.9b) and (2.9c) by a factor of $Z/2$. It may well also be possible to obtain a more general form, one applicable to other atoms or ions, or at least to those atoms and ions for which the ground state has zero total orbital angular momentum.

B. Off-diagonal matrix element

The matrix element that appears in the generalized oscillator strength for the $1\,^1S$-$2\,^1P$ transition in helium is

$$\begin{aligned} \epsilon_{21}(K) &= \langle\phi_2|\exp(i\vec{K}\cdot\vec{r}_1) + \exp(i\vec{K}\cdot\vec{r}_2)|\phi_1\rangle \\ &= 2\langle\phi_2|\exp(i\vec{K}\cdot\vec{r}_1)|\phi_1\rangle, \end{aligned} \tag{2.11a}$$

where $\phi_1 = \phi_1(r_1, r_2, r_{12})$ is again the $1\,^1S$ ground-state wave function, ϕ_2 is the $2\,^1P$ excited-state wave function of helium, and we have used the

fact that both ϕ_1 and ϕ_2 are symmetric under the interchange of coordinates 1 and 2. Without any loss of generality, ϕ_2 can be written in the form

$$\phi_2 = r_1\chi_D(r_1, r_2, r_{12})Y_{10}(\hat{r}_1) + r_2\chi_{EX}(r_1, r_2, r_{12})Y_{10}(\hat{r}_2),$$

where the subscripts D and EX will always denote direct and exchange, respectively, and where

$$\chi_{EX}(r_1, r_2, r_{12}) = \chi_D(r_2, r_1, r_{12}), \tag{2.12}$$

and both χ_D and χ_{EX} remain finite and nonzero as either r_1 or r_2 goes to zero. Expanding the plane wave in partial waves, we have

$$\epsilon_{21}(K) = 2(12\pi)^{1/2}i\langle\phi_2|j_1(Kr_1)Y_{10}(\hat{r}_1)|\phi_1\rangle. \tag{2.11b}$$

This can be rewritten formally as the one-dimensional integral

$$\epsilon_{21}(K) = 2(12\pi)^{1/2}i\int_0^\infty r_1^2 dr_1 j_1(Kr_1)H(r_1), \tag{2.13a}$$

where

$$H(r_1) \equiv \int d\Omega_1 \int d\vec{r}_2 \phi_2^* Y_{10}(\hat{r}_1)\phi_1 \tag{2.13b}$$

is independent of the momentum transfer $\hbar K$. Equation (2.13a) can be integrated by parts successively to get the asymptotic expansion

$$\epsilon_{21}(K) = \frac{4(12\pi)^{1/2}i}{K^3}\sum_{n=0}^{\infty}\frac{(-1)^n(n+1)}{K^{2n}}\left.\frac{d^{2n}H(r_1)}{dr_1^{2n}}\right|_{r_1=0}. \tag{2.14}$$

To obtain the coefficients of the leading terms in the asymptotic expansion (2.14) in terms of ϕ_1 and ϕ_2, we proceed as we did earlier for the diagonal matrix element case, namely, we expand the integrand in (2.13b) as a power series in r_1 and integrate term by term. Since $H(0) = 0$, the leading term in the expansion (2.14) goes as K^{-5}, as expected from Eq. (1.2). The expansion (2.14) can be rewritten as

$$\epsilon_{21} = i(I_D + I_{EX})/(Ka_0)^5 + O(1/(Ka_0)^7), \tag{2.15}$$

where

$$I_D \equiv -64\pi(12\pi)^{1/2}a_0^5\int_0^\infty r_2^2 dr_2 \left.\frac{\partial(\phi_1^*\chi_D)}{\partial r_1}\right|_{r_1=0}, \tag{2.16a}$$

$$I_{EX} \equiv +\frac{64\pi}{3}(12\pi)^{1/2}a_0^5\int_0^\infty r_2^3 dr_2 \left.\frac{\partial^2(\phi_1^*\chi_{EX})}{\partial r_1 \partial r_{12}}\right|_{r_1=0}. \tag{2.16b}$$

The subscripts D and EX denote the direct and exchange character of the integral. I_D and I_{EX}, individually, are the leading coefficients in the asymptotic expansion of

$$\epsilon_{21\,D}(K) = 2i(12\pi)^{1/2}\langle r_1\chi_D Y_{10}(\hat{r}_1)|j_1(Kr_1)Y_{10}(\hat{r}_1)|\phi_1\rangle, \tag{2.17a}$$

and

$$\epsilon_{21\,EX}(K) = 2i(12\pi)^{1/2}\langle r_2\chi_{EX} Y_{10}(\hat{r}_2)|j_1(Kr_1)Y_{10}(\hat{r}_1)|\phi_1\rangle, \tag{2.17b}$$

respectively.

III. SOME NUMERICAL RESULTS FOR I, J, I_D AND I_{EX}

We have calculated numerically the leading coefficients I and J in the asymptotic expansion (2.8), the diagonal matrix element case, and the coefficients I_D and I_{EX} in the asymptotic expansion (2.15), the off-diagonal matrix element case. We have employed approximate wave functions of helium with different numbers of parameters. In particular, 6- and 10-parameter ground-state wave functions were taken from Page,[10] a 20-parameter ground-state wave function from Hart and Herzberg,[11] and a 53-parameter ground-state wave function from Weiss.[12] For the $2\,^1P$ excited state, we ourselves determined 7-, 10-, 20-, and 35-parameter wave functions using the Rayleigh-Ritz energy-minimization procedure; in addition, a 52-parameter $2\,^1P$ excited-state wave function was taken from Weiss.[12] The constants of the various wave functions are given elsewhere.[13]

Table I gives the numerical values of I and J using various ground-state wave functions. The simplest of these wave functions is a Hartree product of hydrogenic wave functions with $Z = \frac{27}{16}$. Pekeris,[14] using his elaborate 1078-parameter ground-state wave function, evaluated the integral appearing in (2.9c). Table II gives numerical estimates of the leading coefficient $(I_D + I_{EX})$ for the off-diagonal matrix element case and for its individual components I_D and I_{EX}, using, firstly, ground-state wave functions and $2\,^1P$ excited-state wave functions with a comparable number of

TABLE I. Coefficients of the leading terms in the asymptotic expansion [see Eq. (2.8)] of the atomic form factor for helium using approximate ground-state wave functions ϕ_1 with different numbers $N(\phi_1)$ of linear parameters; all have one nonlinear parameter.

$N(\phi_1)$	I	J
0	307.55	−6 732.62
6	363.13	−13 165.83
10	363.94	−13 147.36
20	364.21	−13 176.49
53	363.95	−12 718.44
1078	364.01	

TABLE II. Coefficients I_D and I_{EX} of the leading term in the asymptotic expansion [see Eq. (2.15)] of $\epsilon_{21}(K)$ for helium, using approximate ground-state wave functions ϕ_1 and $2\,^1P$ excited-state wave functions ϕ_2 with different numbers $N(\phi_1)$ and $N(\phi_2)$, respectively, of linear parameters. The wave functions with no linear parameters are Hartree products of hydrogenic functions. The closeness in value of the numbers with dashed lines underneath indicates the insensitivity of I_D to the ground-state trial wave function, while the closeness of the numbers with solid lines underneath indicates the insensitivity of I_{EX} to the excited-state trial wave function.

$N(\phi_1)$	$N(\phi_2)$	I_D	I_{EX}	I_D+I_{EX}
0	0	37.95	0	37.95
6	7	46.30	−33.62	12.68
	10	51.48	−33.81	17.67
	20	52.89	−33.17	19.72
	35	60.46	−32.79	27.67
	52	62.51	−32.73	29.78
10	7	46.46	−29.90	16.56
	10	51.65	−30.01	21.64
	20	53.05	−29.37	23.68
	35	60.64	−29.01	31.63
	52	62.70	−28.95	33.75
20	7	46.68	−23.69	22.99
	10	51.86	−23.74	28.12
	20	53.23	−23.10	30.13
	35	60.83	−22.75	38.08
	52	62.89	−22.70	40.19
53	7	46.60	−23.38	23.22
	10	51.77	−23.42	28.35
	20	53.14	−22.78	30.36
	35	60.73	−22.43	38.30
	52	62.78	−22.38	40.40

parameters, and secondly, the ground-state wave functions and $2\,^1P$-state wave functions, which differ significantly in the number of parameters.

Note that $\lim_{K\to\infty} -iK^5a_0^5\epsilon_{21}(K) = I_D + I_{EX}$ and that the integral (2.11b) for $\epsilon_{21}(K)$ can be computer coded for given wave functions for any value of K. Table III gives the values of $-iK^5a_0^5\epsilon_{21}(K)$ for different values of Ka_0. As $K^2a_0^2$ gets larger, the value of $-iK^5a_0^5\epsilon_{21}(K)$ approaches the value I_D+I_{EX} as given in Table II for a given set of wave functions. The integrals $\epsilon_{21\,D}$ and $\epsilon_{21\,EX}$ [see Eq. (2.17)] can also be computer coded. Table III also gives the values of $-i\epsilon_{21\,D}K^5a_0^5$ and $-i\epsilon_{21\,EX}\cdot K^5a_0^5$ for $K^2a_0^2=10^5$, which approach I_D and I_{EX}, respectively, in the asymptotic domain. These results not only provide a check on the values given in Table II, but also give a reasonable estimate of the momentum transfer at which the leading term in the asymptotic behavior is of the accuracy one seeks.

Finally, we note that in the off-diagonal matrix element case, the components I_D and I_{EX} of the leading coefficient I arise from the direct and exchange terms in the $2\,^1P$ excited-state wave function. Looking at the results in Table II, we note that I_D is almost insensitive to the ground-state wave function (see, for example, the numbers with the dashed lines underneath), but varies significantly for a change of the excited-state wave function. The opposite is true for I_{EX}, namely, I_{EX} is almost insensitive to the excited-state wave function (see, for example, the numbers with solid lines underneath) but varies considerably for a change of the ground-state wave function. This observation is also borne out by the results in Table III. Looking at the entries in either Table II or Table III, it is apparent that I_{EX} has nearly

TABLE III. Values of $-i\epsilon_{21}(K)K^5a_0^5$ for increasing values of $K^2a_0^2$. The last two columns give the decomposition of $-i\epsilon_{21}K^5a_0^5$, for $K^2a_0^2=10^5$, into its direct and exchange components.

		$-i\epsilon_{21}(K)K^5a_0^5$			$K^2a_0^2=10^5$	
$N(\phi_1)$	$N(\phi_2)$	$K^2a_0^2=10^3$	$K^2a_0^2=10^4$	$K^2a_0^2=10^5$	$-i\epsilon_{21\,D}K^5a_0^5$	$-i\epsilon_{21\,EX}K^5a_0^5$
6	7	12.86	12.70	12.67	46.29	−33.62
	10	17.49	17.65	17.66	51.47	−33.81
	20	19.27	19.67	19.71	52.87	−33.16
	52	28.64	29.66	29.76	62.49	−32.73
10	7	16.46	16.55	16.56	46.45	−29.89
	10	21.18	21.59	21.63	51.63	−30.00
	20	22.95	23.61	23.67	53.03	−29.36
	52	32.34	33.61	33.73	62.68	−28.95
20	7	22.37	22.93	22.99	46.67	−23.68
	10	27.14	28.02	28.10	51.84	−23.74
	20	28.89	30.00	30.12	53.22	−23.10
	52	38.26	39.99	40.16	62.86	−22.70
53	7	22.45	23.14	23.20	46.58	−23.38
	10	27.22	28.23	28.34	51.75	−23.41
	20	28.96	30.21	30.33	53.12	−22.79

converged to a value close to -23, and I_D has converged to about $+63$. As the number of parameters in the wave function increases, the computer program for ϵ_{21}, or its components $\epsilon_{21\,D}$ and $\epsilon_{21\,EX}$, not only becomes more elaborate but also more time consuming. In such a situation, the procedure for determining the leading coefficient in the asymptotic expansion of ϵ_{21} by taking the large-momentum-transfer limit of $K^5\epsilon_{21}$ is not ideal. This is exactly when the analytic expression (2.16) for the leading coefficient becomes quite useful. Even for quite elaborate wave functions only few terms survive in the wave functions and their derivatives near the origin. (One nevertheless retains the *full* benefit of the effort that went into determining the wave functions.) The program for I_D and I_{EX} is manageable on the computer even for a sophisticated wave function. For example, for $N(\phi_1)=20$ and $N(\phi_2)=52$, the calculation of ϵ_{21} takes approximately 65 sec. on a CDC 6600 computer, whereas the calculation of I_D+I_{EX} with the same numbers of parameters takes only a fraction of a second.

IV. ANALYTIC PROPERTIES OF $\epsilon_{fi}(K)$

As is so often the case, it is useful to extend a real physical variable, in this case K, into the complex plane. One can then use the theory of functions of a complex variable to study the matrix element $\epsilon_{fi}(K)$ defined by Eq. (1.1) and hope to transform some knowledge of the behavior of $\epsilon_{fi}(K)$—the position of its poles, for example—into rather general information about the matrix element, such as the functional form of its dependence upon K. This may enable one to use values of $\epsilon_{fi}(K)$ for some real values of K to obtain estimates of $\epsilon_{fi}(K)$ for other real values of K. We have little to contribute to the formal analysis, but a few remarks may be useful to those who pursue the matter in the future. Furthermore, the remarks will be helpful in guessing at the forms of $\epsilon(K)$ considered below.

Since the integrand of $\epsilon_{fi}(K)$ is finite everywhere in the finite complex K plane, the singularities of $\epsilon_{fi}(K)$ in the finite complex K plane can only come from regions of very large r. Lassettre[15] *assumed* that as the coordinate of a given electron becomes large, one could ignore the possibility that any other coordinate would be comparably large. To simplify the discussion, and in particular the notation, we restrict our considerations for the moment to helium. Further, we take the initial state to be the $1\,^1S$ ground state, characterized as a $(1s)^2$ state, and we take the final state to be the state characterized as the singlet $(1s)(nl)$ state, where nl can be $1s$. The electron with coordinate r_1 will be assumed to be the active electron, and the matrix element $\epsilon_{fi}(K)$ for the $(1s)^2$ to $(1s)(nl)$ transition will be written as $\epsilon^{nl}(K)$. (In particular, $\epsilon^{1s}(K)$ and $\epsilon^{2p}(K)$ are therefore what we previously denoted by $\epsilon_{11}(K)$ and $\epsilon_{21}(K)$, respectively.) The energy of the singlet $(1s)(nl)$ state will be denoted by $E_{He}(1s,nl)$. We assume that

$$\psi_{He}(1s,nl)\sim\psi_{He^+,1s}(r_2)g_{nl}(r_1)P_l(\cos\theta_1)\,,\quad r_1\sim\infty\,.$$

Using the equations satisfied by the helium atom and helium-ion wave functions, and replacing e^2/r_{12} by e^2/r_1, since $r_1\sim\infty$, we find

$$\{T_1-(e^2/r_1)+[l(l+1)\hbar^2/2m\,r_1^2]+(\alpha_{nl}^2\hbar^2/2m)\}\times g_{nl}(r_1)\approx 0\,,\quad r_1\sim\infty\,,\tag{4.1a}$$

where

$$T_1\equiv-\frac{\hbar^2}{2m}\frac{1}{r_1^2}\frac{d}{dr_1}r_1^2\frac{d}{dr_1}\,,\tag{4.1b}$$

and

$$\alpha_{nl}^2\hbar^2/2m\equiv -E_{He}(1s,nl)+[-4(e^2/2a_0)]\,;\tag{4.2}$$

the quantity in square brackets is $E_{He^+}(1s)$. In particular, $\alpha_{1s}^2\hbar^2/2m$ is the ionization energy of the $(1s)^2$ state of helium. It is now entirely trivial to obtain the asymptotic form of $g_{nl}(r_1)$ and thereby to deduce[15] that $\epsilon^{nl}(K)$ has poles at $K=\pm i(\alpha_{1s}+\alpha_{nl})\equiv\pm i\alpha$. That poles exist at these points is almost certain. The question that remains is if there are additional poles.

The transformation

$$t=K/(K^2+\alpha^2)^{1/2}\tag{4.3}$$

maps a singularity-free region of $\epsilon^{nl}(K)$ into the unit circle of the t plane, and since K varies from 0 to ∞ as t varies from 0 to 1, it follows under the assumptions made that an expansion of $\epsilon^{nl}(K)$ as a power series in t will converge for all physically attainable values of K.[15,16] Now in fact even for r_1 large, there is a finite possibility that r_2 can be comparably large.[16] The above analysis may not then be exact, and there may be other singularities[16,17] of $\epsilon^{nl}(K)$. The requirement that the wave functions be antisymmetric may also lead to additional singularities.[16,17] In this last regard we note that it would be useful if, in the course of future calculations of $\epsilon^{nl}(K)$, the direct and exchange contributions were to be separately recorded, as we did in this paper for the generalized oscillator strength for He for the $1\,^1S$ to $2\,^1P$ transition. This might help to determine if the exchange contribution possesses singularities at values of K other than $\pm i\alpha$. [Even if such additional singularities exist, they may have very small residues and/or be far removed from the real axis, and therefore may have a small effect on $\epsilon^{nl}(K)$ for K

real.]

The reader may well have asked himself why we are concerned with the behavior of $\epsilon^{nl}(K)$ for large K; though there will be instances in which $\epsilon^{nl}(K)$ for large K will be of direct interest, for most practical purposes it will be small values of K for which $\epsilon^{nl}(K)$ will be of direct interest. Thus, for example, various cross sections can be expressed as integrals over K of the generalized oscillator strengths, and the contributions to these integrals from large K are quite small. Nevertheless, in an analysis which proceeds within the formalism of the theory of a function of a complex variable, the asymptotic form of $\epsilon^{nl}(K)$ can be of considerable interest. Thus, for example, since $t\sim 1$ as $K\sim\infty$, while

$$1-t^2=\alpha^2/(\alpha^2+K^2)\sim\alpha^2/K^2$$

as $K\sim\infty$, it is clear[15] that if $\epsilon^{nl}(K)$ vanishes as K^{-2d} for $K\sim\infty$, the power series expansion in t of $\epsilon^{nl}(K)$ must be of the particular form

$$\epsilon^{nl}(k)=(1-t^2)^d\sum_0^\infty b_n t^n,$$

(where the sum neither vanishes nor diverges for t close to unity). The factor $(1-t^2)^d$ does not contain any information at $K=0$, where $t=0$ and the factor reduces to unity, but it does contribute to the K dependence of $\epsilon^{nl}(K)$ at low K, even though it originated from a knowledge of the high-K behavior of $\epsilon^{nl}(K)$. (Indeed, for certain transitions in hydrogen, the factor deduced from a knowledge of the high-K behavior gives $\epsilon^{nl}(K)$ *exactly* for all K.)

In the literature, the form of $\epsilon^{nl}(K)$, expressed as a function of t, has sometimes been patterned after its (known) form for an analogous hydrogenlike matrix element, but this viewpoint may be too limited. Thus, for example, the effective Z for hydrogen and hydrogenlike ions is the true Z, and therefore the same for all r, whereas for other atoms, and for helium in particular, an effective Z for large r (important for low K) can be different from an effective Z for small r (important for large K). Since $t\sim 1$ as $K\sim\infty$, the expansion of $\epsilon^{nl}(K)$ as a power series in t can converge very slowly for large K, and since knowledge of $\epsilon^{nl}(K)$ for large K can be useful for small K, one might well consider forms other than power series in t. Figures 1 and 2 show the rapid variation with t, near $t=1$, of the functions $A(t^2)$ and $B(t^2)$, defined below, which are constructed from the form factor $F(K)=\epsilon^{1s}(K)$ and from $\epsilon^{2p}(K)$ by extracting the known t dependence. Thus, we know that $\epsilon^{1s}(K)\sim I/(Ka_0)^4$ for $K\sim\infty$, and we also know that

$$\epsilon^{1s}(K)/2=1-\langle r^2\rangle K^2/3!+\cdots=1-\langle r^2\rangle\, t^2\alpha^2/3!+\cdots \tag{4.4a}$$

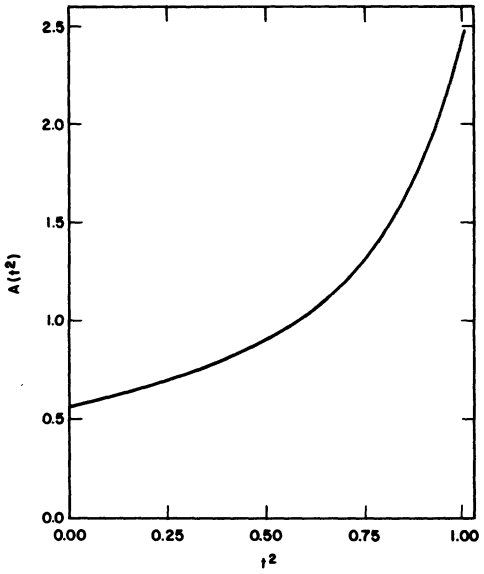

FIG. 1. A plot showing the considerable variation of $A(t^2)$, given by Eq. (4.5b), with t^2, especially near $t=1$.

for small K, where α in Eq. (4.4a) is equal to $2\alpha_{1s}$. This suggests that we write

$$\epsilon^{1s}(K)=2(1-t^2)^2\left(1+\sum_1^\infty d_n(t^2)^n\right). \tag{4.4b}$$

We have therby built in the low-K behavior of $\epsilon^{1s}(K)$ in the sense that Eq. (4.4b) gives $\epsilon^{1s}(K)=2+O(K^2)$; we have built in the coefficient of K^2 even though it will often be reasonably well known. Further, we have not built in the high-K behavior only in the sense that Eq. (4.4b) gives $\epsilon^{1s}(K)\sim\text{const}/K^4$ as $K\sim\infty$. The value of the constant I/a_0^4 has not been built in since for most atoms I will not be known. (The value of I will be built in shortly.) Introducing

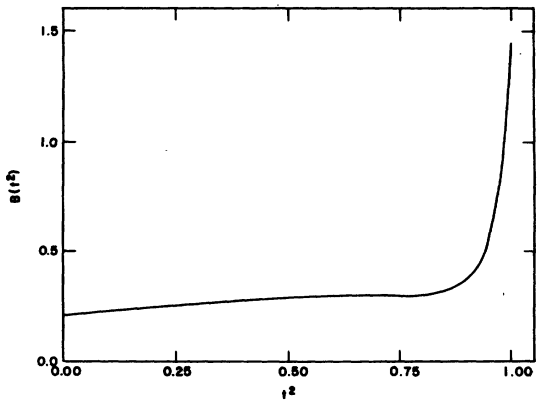

FIG. 2. A plot showing the dramatic variation of $B(t^2)$, given by Eq. (4.6), with t^2 near $t=1$.

$$A(t^2) \equiv \sum_1^\infty \frac{d_n (t^2)^n}{t^2} = d_1 + d_2 t^2 + \cdots , \tag{4.5a}$$

we see from Fig. 1, drawn with the use of computed values[18] of $\epsilon^{1s}(K)$, that

$$A(t^2) = [\tfrac{1}{2}(1-t^2)^{-2}\epsilon^{1s}(K) - 1]/t^2 \tag{4.5b}$$

is rapidly varying near $t = 1$, though it is finite. In fact, upon inserting the asymptotic form for $\epsilon^{1s}(K)$ for $K \sim \infty$ given by Eq. (2.8) into Eq. (4.5b), we find that

$$A(1) = I/2(\alpha a_0)^4 - 1 = 2.4814 . \tag{4.5c}$$

Of course, the series representation for $A(t^2)$ given by Eq. (4.5a) might diverge at $t^2 = 1$ even though $A(1)$ is finite, because $A(t^2)$ might have a pole on the unit circle for t^2 at a point other than $t^2 = 1$. [We note in passing that the value of $\langle r^2 \rangle$ obtained from Eq. (4.4a) by using the known values of $\epsilon^{1s}(K)$ is in excellent agreement with the value obtained directly by Pekeris.[14]] To build in the coefficient of K^{-4}, we write

$$\epsilon^{1s}(K) = 2(1-t^2)^2[1 + A(1)t^2 + t^2(1-t^2)A^*(t^2)], \tag{4.5d}$$

with $A(1)$ given by Eq. (4.5c). Equation (4.5d) gives $\epsilon^{1s}(0) = 2$ *and* $\epsilon^{1s}(K) \sim I/(Ka_0)^4$ as $K \sim \infty$, but a graph of $A^*(t^2)$ as defined by Eq. (4.5d) is not significantly flatter near $t^2 = 1$ than the graph of $A(t^2)$. We note that

$$A^*(t^2) = [A(t^2) - A(1)]/(1-t^2)$$

and, further, as follows by comparing the asymptotic forms of $\epsilon^{1s}(K)$ as defined by Eqs. (4.5d) and (2.8), that

$$A^*(1) = 2 + 3A(1) + [J/(2\alpha^6 a_0^6)] = -7.385 .$$

Similarly, we know that

$$\epsilon^{2p}(K) \sim (I_D + I_{EX})(Ka_0)^{-5}, \quad K \sim \infty$$

and we also know that the dipole oscillator strength $f(0)$ defined by

$$f(0) = \lim_{K \to 0} \frac{2\Delta E}{e^2/a_0} \left| \frac{\epsilon^{2p}(K)}{Ka_0} \right|^2 ,$$

where $\Delta E = E_{He}(1s\,2p) - E_{He}(1s^2)$, is easily obtained experimentally. We rewrite the above equation as

$$\epsilon^{2p}(K) \sim (Ka_0)[\tfrac{1}{2} f(0)(e^2/a_0)/\Delta E]^{1/2} \equiv t\tau, \quad K \sim 0$$

where, noting that $K \sim \alpha t$ for $K \sim 0$,

$$\tau^2 = \tfrac{1}{2}(\alpha a_0)^2 f(0)(e^2/a_0)/\Delta E = 0.6008 ;$$

α is given by $\alpha = \alpha_{1s} + \alpha_{2p}$, where α_{nl} is defined by Eq. (4.2). The forms of $\epsilon^{2p}(K)$ for $K \sim 0$ and for $K \sim \infty$ suggest the form

$$\epsilon^{2p}(K) = \tau t(1-t^2)^{5/2}\left(1 + \sum_1^\infty d_n' t^{2n}\right) .$$

(Note that this expression incorporates the *form* for $K \sim \infty$, but not the numerical coefficient; that will be done shortly. It of course gives the correct behavior for $K \sim 0$.) We now introduce

$$B(t^2) \equiv t^{-2} \sum_1^\infty d_n' t^{2n} = d_1' + d_2' t^2 + \cdots ,$$

so that

$$B(t^2) = t^{-2}\{[(1-t^2)^{-5/2}\epsilon^{2p}(K)/(t\tau)] - 1\}. \tag{4.6}$$

Using known values[19] of $\epsilon^{2p}(K)$, we have plotted $B(t^2)$ in Fig. 2. Here we see an even more rapid variation for t close to 1, so that again we have a series, here for $\epsilon^{2p}(K)$, which is not rapidly converging. We note that the use of Eq. (2.15) in Eq. (4.6) leads to

$$B(1) = (I_D + I_{EX})/\tau(\alpha a_0)^5 - 1 = 1.458 .$$

To build in the correct asymptotic behavior of $\epsilon^{2p}(K)$ as $K \sim \infty$, coefficient and all, we write

$$\epsilon^{2p}(K) = \tau t(1-t^2)^{5/2}[1 + B(1)t^2 + t^2(1-t^2)B^*(t^2)] ,$$

with $B(1)$ defined as just above. The variation of $B^*(t^2)$ near $t^2 = 1$ is unfortunately almost as rapid as the variation of $B(t^2)$ near 1. We note in passing that

$$B^*(t^2) = [B(t^2) - B(1)]/(1-t^2) .$$

Since we have not evaluated the coefficient of the second term in the expansion of ϵ^{2p}, the term analogous to J in the expansion of ϵ^{1s}—compare Eqs. (2.15) and (2.8)—we cannot give the numerical value of $B^*(1)$.

The above analysis, in which the known behavior of $\epsilon^{nl}(K)$ was extracted, is similar to some work done by Rau in a study of the $1\,^1S$ and $2\,^1S$ transition in helium.[20] [One must of course be cautious in using high-K numerical values of matrix elements, especially if, as was the case for Kim and Inokuti, the emphasis in the calculation was on low values of K. The point is that one needs wave functions that are very accurate near the origin to obtain reasonable values for high K, while the determination of the approximate wave function through minimization of the energy in a Rayleigh-Ritz calculation places the emphasis on obtaining a wave function that is good at distances of the order of a_0. There are, nevertheless, two reasons for suspecting that the Kim-Inokuti numbers are reasonably accurate even for somewhat high K. Firstly, the figures plotted in Figs. 1 and 2 are smooth. Secondly, the wave function used by Kim and Inokuti gives as the value of the density at the origin $\rho(0) = 1.8101$, while the value obtained using the elaborate 1078-parameter wave function of Pekeris gives $\rho(0) = 1.8104$. We will assume that the rapid variation of $A(t^2)$ and of $B(t^2)$ near

$t=1$ is not an artifact introduced by inaccuracies in the numerical calculation of $\epsilon(K)$.]

The rapid variation of $A(t^2)$ and $B(t^2)$ near $t=1$ suggests that not all of the "physics" has been extracted; we may need to know more about $\epsilon^{nl}(K)$ than (i) its behavior at very low (real) K, (ii) its behavior at very high (real) K, and (iii) the fact that it has poles at $K=\pm i\alpha$. [Not on theoretical grounds, but simply from the poles of $A(t^2)$ and $B(t^2)$, one might suspect that $\epsilon^{nl}(K)$ has poles at values of t close to $|t|=1$ and of magnitude greater than unity.] Padé approximants are very flexible forms, which, in particular, can readily account for singularities outside the domain of convergence, and we therefore consider Padé approximants for $A(t^2)$ and $B(t^2)$, defined by Eqs. (4.5) and (4.6), respectively, for a few different assumptions. Clearly, one is free to use any available information. For example, in the study of the form factor of a given atom—we will perform our numerical analysis for helium but much of the analysis is applicable to other atoms—the $\langle r^2\rangle$ which appears in the second term in the low-K (or low-t) expansion can be reasonably well estimated if one has available an experimental value of the diamagnetic susceptibility of the atom. Furthermore, in some unpublished work by the authors and Rau, it is shown that, not surprisingly, a knowledge of the behavior of the atomic wave function for one of the electron coordinates very small gives information about the behavior of $\epsilon(K)$ for $K\sim\infty$. In particular, it should be possible for a number of atoms to estimate the ratio of the second to the first numerical coefficients of the expansion of $\epsilon(K)$ as a power series in $1/(Ka_0)^2$. We now return to our analysis of helium, assuming that we know only something of the behavior of $\epsilon(K)$ at $K\sim 0$ and $K\sim\infty$.

From a knowledge of the diamagnetic susceptibility of He, we know $A(0)=0.5618$. Also from a knowledge of the numerical values of the leading coefficients I and J in the asymptotic expansion of $\epsilon^{1s}(K)$, we deduce $A(1)=2.4814$ and $A'(1)=7.3834$, where the prime denotes the derivative with respect to t^2. Using these values we can construct a Padé approximant, with three parameters, of the form

$$A(t^2)=(0.5618+0.0834\,t^2)/(1-0.7400\,t^2)\,,$$

which reproduces the values of $A(t^2)$ to within 7% for all values of t between 0 and 1.

On the other hand, using only the knowledge of $A(0)$ and the ratio J/I of the two leading coefficients in the asymptotic expansion of $\epsilon^{1s}(K)$, one can construct a Padé approximant, with two parameters, of the form

$$A(t^2)=0.5618/(1-0.9340\,t^2)\,,$$

which reproduces $A(t^2)$ very well for low values of t but can be as much as 75% off for t close to 1. In constructing a Padé approximant for $B(t^2)$, we assume that we know only that $B(0)=0.210$, $B(1)=1.458$, and $B'(1)=29.44$. The approximant

$$B(t^2)=(0.210-0.086\,t^2)/(1-0.915\,t^2)$$

gives $B(t^2)$ within 3% for $t<0.5$, but is as much as 50% off for t close to 1.

While our three-parameter Padé approximant for $A(t^2)$ was not bad, it is clear that in general it would be desirable to have available more information about $\epsilon(K)$. One could take a fundamental approach and attempt to obtain some deeper theoretical insights into the structure of $\epsilon(K)$; as noted above, for example, there can be other singularities originating in exchange effects or in the effects of two electrons being simultaneously at great distances. We will here, however, restrict ourselves to a much less basic approach. In the remainder of the paper we examine the form of the wave functions for one coordinate small to obtain at least rough estimates of the ratios not only of the first two coefficients but of the first few coefficients in the expansion in powers of $1/(Ka_0)^2$ of $\epsilon(K)$.

The point to be emphasized is that it is possible, as we will now show, to obtain information about $\epsilon^{nl}(K)$ for $K\sim\infty$ beyond the form of the K dependence, and that this information may also be useful in studying the low-K dependence of $\epsilon^{nl}(K)$. To study the very-high-K domain, it is necessary to study the region of very small r_1. We ignore the possibility that the second electron is at comparably small distances, and, since the active electron is the one with coordinate r_1 so that the outer electron sees a unit charge, we write

$$\psi_{\mathrm{He}}(1s,nl)\sim\psi_{\mathrm{H},1s}(r_2)G_{nl}(r_1)(-i)^l P_l(\cos\theta_1),\quad r_1\sim 0\,. \tag{4.7}$$

Using the equations satisfied by the helium and hydrogen functions and approximating e^2/r_{12} by e^2/r_2, we find

$$[T_{1l}-(2e^2/r_1)+(q_{nl}^2\hbar^2/2m)]G_{nl}(r_1)\approx 0,\quad r_1\sim 0\,, \tag{4.8}$$

where

$$T_{1l}=-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr_1^2}+\frac{2}{r_1}\frac{d}{dr_1}-\frac{l(l+1)}{r_1^2}\right),$$

and where

$$q_{nl}^2\hbar^2/2m\equiv -E_{\mathrm{He}}(1s,nl)+[-(e^2/2a_0)]\,. \tag{4.9}$$

We choose $G_{nl}(r_1)$ to be regular at the origin. The

normalization of $G_{nl}(r_1)$ is, of course, not determined by the equation it satisfies, and, in fact, since the energy in Eq. (4.8) is not an eigenvalue of the equation, $G_{nl}(r_1)$ will diverge at infinity. However, only the value of G_{nl} in the neighborhood of the origin will concern us. G_{nl} is simply the Coulomb function (proportional to the hypergeometric function), that is,

$$G_{nl}(r_1)=N_{nl}r_1^l\exp(-q_{nl}r_1)\,{}_1F_1(l+1-[2/(q_{nl}a_0)],\ 2l+2,\ 2q_{nl}r_1),$$

with the normalization constant N_{nl} unknown. (Though his derivation is not rigorous, Lassettre's deduction[15] that $\epsilon^{nl}(K)$ can be expanded in a power series in t for all K may be exact, for although exchange effects and the effect of two electrons being at great distances will almost surely introduce new singularities, they can be expected to be introduced at points in the K plane such that the region in the K plane mapped into the unit circle in the t plane still contains no singularities. On the other hand, as will be discussed later, the results obtained below are almost surely not exact. Note, though, that Lassettre's results, even if *not* exact, can still be useful if, for example, the additional singularities are far from the real axis and have weak strengths. Correspondingly, the results to be obtained below can be useful even though they are not exact.)

Using Eq. (4.7) to approximate the initial and final states, integrating over r_2, and dropping the subscript on r_1, we immediately obtain

$$\begin{aligned}\epsilon^{nl}(K)&\sim 2N_{1s}N_{nl}\int' d\vec{r}\,e^{-q_{1s}r}\,{}_1F_1(1-[2/(q_{1s}a_0)],2,2q_{1s}r)\,e^{i\vec{K}\cdot\vec{r}}r^l e^{-q_{nl}r}\\&\quad\times{}_1F_1(l+1-[2/(q_{nl}a_0)],2l+2,2q_{nl}r)(-i)^l P_l(\cos\theta)\\&=8\pi N_{1s}N_{nl}\int' dr\,r^{l+2}e^{-(q_{1s}+q_{nl})r}j_l(Kr)\,{}_1F_1(\cdots)\,{}_1F_1(\cdots),\qquad K\sim\infty,\end{aligned}\tag{4.10}$$

where the prime denotes the restriction of the region of integration to $0\le r\le R_1$, where $1/K\ll R_1\ll\frac{1}{2}a_0$. The lower limit guarantees, for fixed K, that the region giving the dominant contribution has been included, and the upper limit is to guarantee that Eq. (4.7) represents a good approximation. In fact, by retaining the exponentially decaying factors in Eq. (4.10), we can extend the upper limit of integration to infinity, and we can integrate term by term after expanding the hypergeometric functions in power series. We immediately obtain

$$\begin{aligned}\epsilon^{nl}(K)\sim 8\pi N_{1s}N_{nl}&\frac{(2a_0)^{l+3}}{(2l+2)}\Gamma(l+3)\\&\times\left\{\frac{1}{(Ka_0)^{l+4}}-\left[\frac{1}{3}(q_{1s}a_0)^2(2l+5)+(q_{nl}a_0)^2\left(\frac{3}{2}+\frac{2}{l+2}-\frac{5}{2}\,\frac{1}{2l+3}\right)+8\left(\frac{l+7}{6}-\frac{1}{l+2}+\frac{5}{2l+3}\right)\right]\Big/(Ka_0)^{l+6}+\cdots\right\}.\end{aligned}\tag{4.11}$$

In particular, we have

$$\epsilon^{ns}(K)\sim 8\pi N_{1s}N_{ns}(2a_0)^3\{1/(Ka_0)^4-\tfrac{1}{3}[5(q_{1s}a_0)^2+5(q_{ns}a_0)^2+56]/(Ka_0)^6+\cdots\},\tag{4.12a}$$

$$\epsilon^{np}(K)\sim 12\pi N_{1s}N_{np}(2a_0)^4\{1/(Ka_0)^5-\tfrac{1}{3}[7(q_{1s}a_0)^2+5(q_{np}a_0)^2+48]/(Ka_0)^7+\cdots\},\tag{4.12b}$$

$$\epsilon^{nd}(K)\sim 32\pi N_{1s}N_{nd}(2a_0)^5\{1/(Ka_0)^6-\tfrac{1}{14}[42(q_{1s}a_0)^2+23(q_{nd}a_0)^2+220]/(Ka_0)^8+\cdots\}.\tag{4.12c}$$

We note parenthetically that if we use the approximation given by Eq. (4.7) to replace $\phi_1(r_1,r_2,r_{12})$ in in Eqs. (2.9) and (2.10), these equations generate identically the same result as, for $n=1$, the first two terms in Eq. (4.12a).

Equations (4.12) cannot be used to check on the value of the leading coefficient unless the normalization constants happen to be reasonably well known, but we can check on the accuracy of Eq. (4.12a) by computing the ratio of the coefficients of the first two terms of $\epsilon^{1s}(K)$, which turns out to be -34.69, and comparing with the ratios -21.89, -36.26, -36.13, -36.18, and -34.95 obtained from Table I; we might characterize the value obtained from Table I as -35 ± 1. The agreement is quite good and the ratio obtained from Eq. (4.12a) might be exact. One can surely not expect Eq. (4.11) to generate *all* coefficients in the asymptotic expansion of $\epsilon^{nl}(K)$ in powers of $1/K$ exactly. Thus, the outer electron will affect the expansion in powers

of r_1 of the wave function (for r_1 small) of the inner electron, and only some of the effect will be built in via the subtraction of the energy of the second electron (for r_1 very small) in the determination of q_{nl}.

Note that a rough estimate of the ratio of the coefficients of the first two terms in the asymptotic expansion of $\epsilon^{nl}(K)$ can be obtained by completely ignoring all effects of the outer electron on the wave function of the inner electron. $G_{nl}(r)$ would then be the hydrogenic (normalizable) wave function. If, to take a simple example, we consider $l=n-1$, we have

$$\epsilon^{n,n-1}(K) \sim \text{const}\int_0^\infty r^{n-1}\exp\left(\frac{-2r}{na_0}\right)j_{n-1}(Kr)\exp\left(\frac{-2r}{a_0}\right)r^2\,dr$$
$$= \text{const}\,\frac{2^{n+1}\Gamma(n+2)}{a_0 n K^{n+3}}\left(1-\frac{4(n+1)^3}{n^2(Ka_0)^2}+\cdots\right). \tag{4.13a}$$

The ratio under consideration is therefore

$$\mathcal{R} = -4(n+1)^3/n^2. \tag{4.13b}$$

In Table IV, we compare the ratio of the coefficients of the first two terms in the asymptotic expansion of $\epsilon^{nl}(K)$, for a few values of n and l, as obtained from Eq. (4.11), Eq. (4.13b), and the numerical values of the form factor and the generalized oscillator strengths. In particular, the numerical data of Kim and Inokuti[18, 19, 21] is fitted to the first three terms in the expansion of $\epsilon^{nl}(K)$ to obtain this ratio.

It should be clear that some of the discussion above might possibly be taken over to heavy atoms, and some can definitely not be taken over. One does not have extremely accurate wave functions for heavier atoms, and often one cannot therefore obtain accurate estimates of the leading coefficient I, but the ratio of the coefficients of the first two terms in the asymptotic expansion of $\epsilon_{fi}(K)$ can, at least in principle, often be obtained by straightforward extension of the above arguments. Consider, for example, the matrix element $\epsilon_{fi}(K)$ for Li, with i the ground state, characterized as a $(1s)^2(2s)$ state, and with f the $(1s)^2(2p)$ excited state. Defining q_{nl} and $\epsilon^{nl}(K)$ in analogy to the definition for helium, one finds

$$(q_{2s})^2\hbar^2/2m = E_{\text{He}}[(1s)^2] - E_{\text{Li}}[(1s)^2 2s]$$

and

$$(q_{2p})^2\hbar^2/2m = E_{\text{He}}[(1s)^2] - E_{\text{Li}}[(1s)^2 2p].$$

From Eq. (4.11), we immediately obtain

$$\epsilon^{2p}(K) = [\text{const}/(Ka_0)^5] \times\{1-\tfrac{1}{3}[7(q_{2s}a_0)^2+5(q_{2p}a_0)^2+48]/(Ka_0)^2+\cdots\}.$$

It would be nice to be able to compare the ratio 52.37 of the coefficients of the leading two terms with the value determined numerically by fitting the generalized oscillator strengths data for $(1s^2)(2p)\,^2P \rightarrow (1s^2)(2s)\,^2S$ transition in Li; unfortunately, the codes presently used in numerically calculations give such large round-off errors that useful results have not been obtained for the high values of K under consideration in the present discussion.

It should also be clear that one is free to use any available information. Thus, for example, in the study of a form factor, the $\langle r^2\rangle$ which appears in the second term in the low-K (or low-t) expansion can be reasonably well estimated if one has available an experimental value of the diamagnetic susceptibility of the atom under study.

After we had completed our numerical studies, it was called to our attention that Lassettre has, in a one-particle model, found[22] that there are many singularities other than the two at $K=\pm i\alpha$. He points out that the results he obtained are not mathematically rigorous, having been obtained in a one-particle model. Nevertheless, the model uses a one-body potential which is of the form an equivalent one-body potential, in a many-body problem, can be expected to assume, and the form of his results is thereby quite believable. Roughly speaking, the equivalent one-body potential for an electron in a neutral atom, for the electron far from the nucleus, is chosen to be $(-e^2/r)+U(r)$, with $U(r)$ a superposition of exponential potentials. (The exponential terms arise because, for large but fixed r, some of the inner electrons can lie beyond r, so that one does not have complete shielding.) Then the wave function $\psi(r)$ for the electron, for r very large, should not only have the term originally used by Lassettre, an exponential with an exponent defined by the binding energy, but additional exponential terms, with exponents representing more rapid decay. These

TABLE IV. The ratio of the coefficients J/I of the leading two terms in the asymptotic expansion of $\epsilon^{nl}(K)$ for helium using Eq. (4.11), Eq. (4.13b), and numerical data of Kim and Inokuti fitted to the first three terms in the expansion of $\epsilon^{nl}(K)$.

	$-J/I$		
$(1s)(nl)$	Eq. (4.11)	Eq. (4.13b)	Kim–Inokuti [a]
$(1s)^2$ $1\,^1S$	34.69	32.00	31.36
$(1s)(2s)$ $2\,^1S$	32.17		39.42
$(1s)(3s)$ $3\,^1S$	31.88		40.24
$(1s)(2p)$ $2\,^1P$	32.63	27.00	40.68
$(1s)(3p)$ $3\,^1P$	32.40		34.17
$(1s)(3d)$ $3\,^1D$	35.25	28.44	27.13

[a] References 18, 19, and 21.

generate poles which are also on the imaginary axis, and at greater distances from the origin; the nearest singularity—actually a pair of singularities—remains that determined by the binding energy, and the transformation originally used by Lassettre[15] continues to generate a convergent power series in t. Clearly, however, it would be interesting to see if building in the new singularities could speed the rate of convergence. Lassettre also considered singularities arising from exchange effects.[22]

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