Total Cross Sections for Inelastic Scattering of Charged Particles by Atoms and Molecules. II. Negative Hydrogen Ion*

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The sum rule for the Bethe inelastic-scattering cross sections is applied to the negative hydrogen ion, for which it yields the asymptotic total cross section for electron detachment by charged-particle impact. The calculation requires knowledge of two properties of H^-: the incoherent-scattering function, which is computed from several different ground-state wave functions, and the oscillator-strength distribution, which is deduced from a variety of experimental and theoretical data. The resulting detachment cross section for electron impact, including all final H-atom states, is $\sigma_{\text{tot}} = 4\pi a_0^2 (R/T)[7.484 \ln(T/R) + 25.3 \pm 1.5]$, where a_0 is the Bohr radius and T/R the incident energy in rydbergs. Our result is consistent with the experimental data of Dance, Harrison, and Rundel, but incompatible with those of Tisone and Branscomb. A tabulation of the incoherent-scattering function and the atomic form factor is also given.

I. INTRODUCTION

Electron detachment from the negative hydrogen ion by electron impact has been the subject of many experimental and theoretical investigations, in part because of its relevance to solar and stellar opacities. However, current understanding still appears to be unsatisfactory. Of the theoretical schemes so far published,[1–5] some give widely different results, and two recent sets of experimental data[6,7] are discordant in their asymptotic behavior at high incident velocities.

As we have shown in Paper I of this series,[8] the asymptotic total cross section for inelastic scattering, namely σ_{tot}, the sum of all the Bethe inelastic-scattering cross sections for fast charged-particle impact, can be evaluated by use of a sum rule. Because H^- possesses no bound excited state below the first detachment threshold, σ_{tot} in this case is the total cross section for detachment; it includes detachment resulting in any final state of atomic hydrogen—excited and ionized states as well as ground state. Use of the Bethe theory implies neglect of the Coulomb interaction between the incident particle and the net charge of H^-, but this simplification is expected to be permissible for sufficiently high incident velocities. The use of our sum rule dispenses with explicit calculation of continuum wave functions; instead it requires knowledge of two accessible properties of H^-: the distribution of optical (dipole) oscillator strength df/dE over excitation energy E, and the incoherent-scattering function $S_{\text{inc}}(K)$ as a function of momentum transfer $K\hbar$. We have constructed df/dE using both theoretical and experimental data and the optical sum rules. We have computed $S_{\text{inc}}(K)$ from different approximate ground-state wave functions. [The resulting $S_{\text{inc}}(K)$, together with a related property, the atomic form factor $F(K)$, is given in Appendix I for use in x-ray physics.]

Our effort is directed to the best possible determination of the asymptotic cross section, an aspect that, in the literature, has been treated only casually or as a matter of secondary concern. Indeed, most of the earlier theoretical studies, motivated primarily by interest in lower-velocity regions, have explored causes of failure of the first Born approximation, and all have failed to exploit it fully within the range of its validity.[1–5]

II. THEORY

As shown in Paper I, the total cross section σ_{tot} for inelastic scattering of a particle with charge ze and sufficiently great (but nonrelativistic) velocity v by an atom can be written as

$$\sigma_{\text{tot}} = 4\pi a_0^2 z^2 (R/T) M_{\text{tot}}^2 \ln(4c_{\text{tot}} T/R), \tag{1}$$

where a_0 is the Bohr radius, R the rydberg energy, and $T = \frac{1}{2}mv^2$, m being the *electron* mass. Of the two atomic properties M_{tot}^2 and c_{tot} the former is simply an optical property, the total dipole matrix element squared (in atomic units), and can be evaluated from

$$M_{\text{tot}}^2 = \langle(\vec{r}_1 + \vec{r}_2)^2\rangle/(3a_0^2), \tag{2}$$

where $\vec{r}_1$ and $\vec{r}_2$ are positions of electrons in H^- and $\langle\ \rangle$ denotes a ground-state expectation value. Evaluation of the less familiar parameter c_{tot} by

$$M_{\text{tot}}^2 \ln c_{\text{tot}} = -2L(-1) + I_1 - I_2 \tag{3}$$

is made possible by the sum rule. Here $L(-1)$ is another optical quantity, which for H^- takes the form

$$L(-1) = \int_{E_1}^{\infty} (df/dE)(R/E)\ln(E/R)dE, \tag{4}$$

where E_1 is the first detachment threshold and I_1 and I_2 are integrals involving $S_{\text{inc}}(K)$ [defined by Eqs. (A1) and (A2) in Appendix I]:

$$I_1 = \int_1^{\infty} 2S_{\text{inc}}(K)\, d(Ka_0)^{-4} d(Ka_0)^2, \tag{5}$$

$$I_2 = \int_0^1 [M_{\text{tot}}^2 - 2S_{\text{inc}}(K)/(Ka_0)^2] \times d(Ka_0)^{-2} d(Ka_0)^2. \tag{6}$$

In order to have some basis for assessing the accuracy of the final results, we have calculated M_{tot}^2 and $S_{\text{inc}}(K)$, and thence I_1 and I_2, from eight different wave functions.[9-14] The computational method has already been described in connection with our earlier work on the helium atom.[15,16] The resulting M_{tot}^2, I_1, and I_2 are shown in Table I, together with additional information for comparison. (See Sec. III for the "Ohmura" model.") The uncertainty in the value of M_{tot}^2 as calculated by Pekeris[17] is, for our purpose, inappreciable. As noted in the case of He,[8] an improvement in terms of total energy does not necessarily imply an improvement in other quantities such as M_{tot}^2. Actually, the values of M_{tot}^2 in the present case converge toward the best Pekeris value much more slowly than for He (see Table I of Paper I). This tendency is basically due to the fact that H^- is dynamically more complicated because of its loose structure, and that currently available Hylleraas wave functions with moderate numbers of terms are still not sufficiently accurate for this purpose. Indeed, the 20-term Hylleraas wave function[14] seems hardly more advantageous than the 11-term Hylleraas wave function,[13] presumably because the choice of terms in the former was biased for the best result in He.

The trend of I_1 and I_2 as the wave function is improved is similar to the trend with He.[8] The convergence of I_2 is again slower than that of I_1, owing to the circumstance that I_2 depends most strongly on $S_{\text{inc}}(K)$ for small Ka_0, which in turn reflects the elusive behavior of the wave function at large r. Conclusive evaluation of $I_1 - I_2$ would require a highly refined wave function such as the Pekeris (444-term) wave function.[17] The use of such an accurate wave function, however, is deferred until a correspondingly accurate evaluation of $L(-1)$ (discussed below) becomes feasible. Instead, we can estimate an "accurate" value of $I_1 - I_2$ by extrapolating the data from superior wave functions in Table I. As illustrated in Fig. 1, the plot of $I_1 - I_2$ versus M_{tot}^2 is smooth, and yields $I_1 - I_2 = -10.5 \pm 0.5$ for $M_{tot}^2 = 7.484$.

Although the Hartree-Fock wave function[9] fails to give a positive electron affinity for the hydrogen atom, its M_{tot}^2, I_1, and I_2 values are comparable to those of the six-term Hylleraas wave function. The Eckart (or open-shell) wave function[11] yields unrealistic values of M_{tot}^2 and I_2, presumably because of its inaccurate behavior at large r.

As was noted in Paper I, $L(-1)$ can be determined by two different methods—directly from df/dE, or by differentiating the moment

$$S(\mu) = \int_{E_1}^{\infty} (df/dE)(E/R)^{\mu} dE \tag{7}$$

at $\mu = -1$. [Notice that $S(-1)$ is equal to M_{tot}^2, given in alternative form by Eq. (2).] In the case of He, the oscillator-strength distribution is well known, and the two methods yield closely agreeing values of $L(-1)$.[8] For H^-, however, the situation is different. Presently available data, experimental[18-21] and theoretical,[22-27] are limited in many respects. First, experimental data are confined to the visible spectral region. Second, most theoretical data, except for those of Macek,[27] are restricted to excitation energies below $2R$. Third, most calculations do not include transitions resulting in an excited or ionized hydrogen atom.[26,27]

TABLE I. Values of M_{tot}^2, I_1, and I_2 of H^-.

Wave function	Total Energy (rydbergs)	M_{tot}^2	I_1	I_2
Exponential[a]	-0.945 31	4.231	1.865	3.754
Hartree-Fock[9]	-0.975 859	6.274	1.877	8.005
2-term Hylleraas[10]	-1.017 56	3.655	1.790	3.090
Eckart[11]	-1.026 60	11.34	1.811	23.01
3-term Hylleraas[10]	-1.050 6	5.451	1.789	6.718
6-term Hylleraas[12]	-1.052 92	5.9580	1.7868	7.9833
11-term Hylleraas[13]	-1.055 118	7.2001	1.7873	11.420
20-term Hylleraas[14]	-1.055 289 34	7.1139	1.7877	11.153
Pekeris[b]	-1.055 502 03	7.484 26		
The Ohmura model[c]		7.958	2.217	11.68

[a] $\psi \sim \exp[-\zeta(r_1 + r_2)]$, $\zeta = \frac{11}{16} a_0^{-1}$.

[b] See Ref. 17; "Extrapolated values" are quoted here.

[c] See Sec. III.

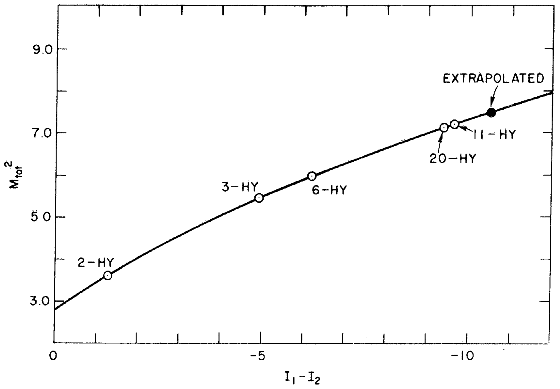

FIG. 1. Extrapolation of I_1-I_2. The ordinate at the extrapolated value of I_1-I_2 is the Pekeris value $M_{tot}^2 = 7.484$. An n-term Hylleraas wave function is denoted by n-HY.

Furthermore, the moment $S(\mu)$ varies so rapidly near $\mu=-1$ that the slope there cannot be determined solely from a few values of $S(\mu)$ for integral μ, to an accuracy better than 20%. To obtain a reliable value of $L(-1)$, we have therefore performed a detailed analysis of theoretical and experimental data and obtained a complete oscillator-strength distribution. This is primarily based on the calculations of Geltman[22] and of Doughty, Fraser, and McEachran,[23] but it is adjusted so as to reproduce all of the accurately known values of $S(\mu)$. Details of this analysis are given elsewhere.[28–30] Table II summarizes the quantities derived from the distribution and compares them with other information. (See Sec. III for the "Ohmura model.") The uncertainty in the resulting value, $L(-1)=-12.7$, is believed to be less than 5%.

III. RESULT AND DISCUSSION

The calculation described above leads to $M_{tot}^2 \times \ln c_{tot} = 14.9 \pm 1.5$, and thence to

$$\sigma_{tot} = 4\pi a_0^2 z^2 (R/T)[7.484 \ln(T/R) + 25.3 \pm 1.5]. \tag{8}$$

This result applies asymptotically for any charged particle, as long as the particle may be regarded as structureless. But the velocity at which the asymptotic behavior is attained, to a definite precision, can depend substantially on the kind of the particle, inasmuch as breakdown of the basic theoretical framework can stem from a variety of causes.

The best way to depict Eq. (8) is to plot $(T/R) \times \sigma_{tot}/(4\pi a_0^2 z^2)$ against $\ln(T/R)$, as shown in Fig. 2. For comparison, experimental data for electron impact obtained by Tisone and Branscomb,[6] and by Dance, Harrison, and Rundel[7] are also shown in Fig. 2. Two qualifications should be borne in mind in judging this comparison. In the first place, neither experiment was designed to detect double detachment resulting in H^+, whereas the theoretical result includes it. Second, no allowance for the Coulomb distortion was made in the calculation. Although a definite estimate of

TABLE II. Values of $S(\mu)$ and $L(\mu)$ of H^-

	$S(\mu)$					$L(\mu)$	
μ	Accurate[a]	Doughty *et al.*[b]	Bell and Kingston[c]	Ohmura model[d]	From adopted df/dE	Ohmura model[d]	From adopted df/dE
2	5.514 157				5.839		14.69
1	1.495 015				1.500		0.6045
0	2				1.977		−1.742
−1	7.484 26	7.10	7.35	7.96	7.486	−13.3	−12.70
−2	51.48	50.5	51.3	53.8	51.21	−112	−107.5
−3	500± 40	465	463	484	467.0	-1.11×10^3	−1075
−4				5.09×10^3	4969	-1.23×10^4	-1.202×10^4
−5				5.90×10^4		-1.47×10^5	
−6				7.30×10^5		-1.86×10^6	

[a] The accurate values of $S(2)$, $S(1)$, and $S(-1)$ were calculated by C. L. Pekeris (Ref. 17), $S(-2)$ from the dipole polarizability [K. T. Chung and R. P. Hurst, Phys. Rev. 152, 35 (1966)], and $S(-3)$ by C. Schwartz (unpublished, quoted in Refs. 22 and 23). Also, see Ref. 30.

[b] The "velocity" results of Ref. 23. Double excitations not included.

[c] The "length" results of Ref. 24. Double excitations not included.

[d] Equations (11) and (12).

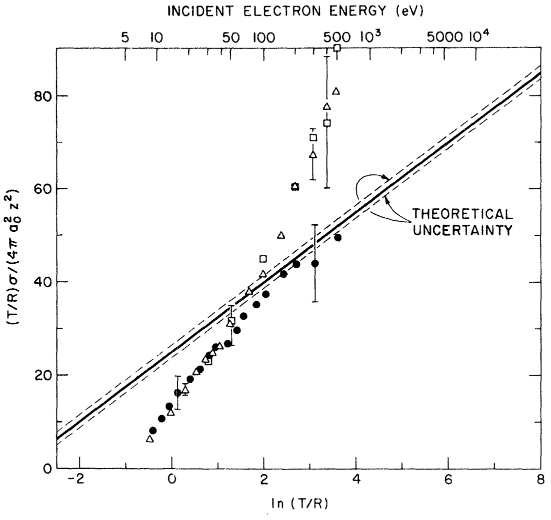

FIG. 2. Cross sections for electron detachment of H^- by charged-particle impact. Theory gives the universal straight line for any charged particle of charge ze. The uncertainty of the line is independent of incident velocities. The dots (●) represent electron-impact data of Dance, Harrison, and Rundel (Ref. 7), the squares (□) those of Tisone and Branscomb (Ref. 6a) and the triangles (Δ) those recently obtained also by Tisone and Branscomb (Ref. 6b). All experimental data exclude double detachment. Error bars are attached only to representative experimental points. (None of the experimental points plotted here, in contrast to Fig. 9 of Ref. 7, is corrected for the "Coulomb effect.") The (nonlinear) scale of incident energies for electrons and positrons is shown at the top.

the effect of the Coulomb distortion is difficult at present, it is plausible that this effect will vanish asymptotically at high velocities. The data of Dance, Harrison, and Rundel are consistent with our result, and interestingly exhibit that familiar trend in approaching the asymptote which is usually found in cross sections for excitation and ionization of neutral atoms and molecules.[31] Further, this apparent agreement implies relative insignificance of double detachment in this instance. In contrast, the data of Tisone and Branscomb are incompatible with our result. We cannot, however, entirely exclude a remote possibility that the incident electron velocity corresponding to some 500 eV should still fall short of the Bethe asymptotic limit. Further experimental work, in particular covering a wider range of incident energies, is desirable to clarify the current inconsistency of measurements in the asymptotic region.

We now discuss previous theoretical studies in relation to our work. The calculation of McDowell and Williamson[2] also utilizes oscillator strengths, but differs from our work in attempting to obtain the cross section below the asymptotic region by a modification of the Bethe theory. Their cross section includes contributions from single detachment only; at higher velocities, it falls slightly below the experimental data of Dance, Harrison, and Rundel, and thus is consistent with our result.

Smirnov and Chibisov[5] formulated a semiclassical impact-parameter treatment, and for the description of H^- used a one-electron model, originally due to Ohmura and Ohmura,[32] and further explored by Armstrong[33] and by Demkov and Drukarev.[34] The Ohmura model is based on recognition that the loose structure of H^- must give rise to the oscillator-strength distribution predominantly concentrated at low E, where it is essentially determined by electronic structure at large r. The detachment cross section obtained by Smirnov and Chibisov includes contributions of double excitation resulting in an excited or ionized hydrogen atom, and asymptotically has the same mathematical form as ours. In their Eq. (31), however, the constant in front of the logarithm seems to contain an erroneous factor of 2. The constant inside the logarithm was evaluated by choosing, as is customary in such a treatment, a cutoff impact parameter, which unavoidably contains some ambiguity.

The simplicity of the Ohmura model permits analytical evaluation of σ_{tot} by use of our theory. The model one-electron wave function[32–34]

$$u_0 = (\gamma/2\pi a_0)^{\frac{1}{2}} r^{-1} e^{-\gamma r/a_0}, \tag{9}$$

with $\gamma^2 = 0.055502$ (the electron affinity in rydbergs of atomic hydrogen[17]) and with a normalization factor (for two electrons) $A = (2.65)^{1/2}$, gives

$$2S_{\text{inc}}(K) = A^2[1-(2\gamma/Ka_0)^2 \arctan^2(Ka_0/2\gamma)], \tag{10}$$

and thence I_1 and I_2 in the last row of Table I. The fact that the value of I_2 is comparable to our most accurate result, while the value of I_1 differs considerably, stems from the emphasis of the model on the correct description of electronic structure at large r. The moments $S(\mu)$ of the oscillator-strength distribution for negative μ can also be calculated analytically, as shown in Appendix II. The result is

$$S(\mu) = [2^{2\mu+1}(-2\mu)!/(-\mu)!(2-\mu)!](A\gamma^{\mu})^2. \tag{11}$$

Assuming the analyticity of $S(\mu)$ with respect to μ, one replaces factorials by Γ functions and differentiates Eq. (11) to obtain

$$L(\mu) = \frac{dS(\mu)}{d\mu} = [-2\psi(1-2\mu) + \psi(1-\mu) + \psi(3-\mu) + 2\ln(2\gamma)]S(\mu), \tag{12}$$

where ψ denotes the logarithmic derivative of the Γ function. Some numerical values of $S(\mu)$ and $L(\mu)$ from Eqs. (11) and (12) are given in Table II; they are in reasonable agreement with the data from our adopted df/dE. Inserting the values of I_1, I_2, and $L(-1)$ in Eq. (3), one obtains $M_{\text{tot}}^2 \ln c_{\text{tot}} = 17.15$. Thus, the Ohmura model leads, together with $M_{\text{tot}}^2 = S(-1) = 7.96$ (Table II), to

$$\sigma_{\text{tot}}=4\pi a_0{}^2z^2(R/T)[7.96\ln(T/R)+28.2], \tag{13}$$

in excellent agreement with our earlier result [Eq. (8)]. Such an agreement illustrates wide applicability of this highly simplified model.

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APPENDIX I. ATOMIC FOR FACTOR AND INCOHERENT-SCATTERING FUNCTION OF H⁻

The functions $F(K)$ and $S_{\text{inc}}(K)$ are defined by

$$F(K)=\langle e^{i\vec{K}\cdot\vec{r}_1}+e^{i\vec{K}\cdot\vec{r}_2}\rangle, \tag{A1}$$

and $$S_{\text{inc}}(K)=\tfrac{1}{2}[\langle|e^{i\vec{K}\cdot\vec{r}_1}+e^{i\vec{K}\cdot\vec{r}_2}|^2\rangle-|F(K)|^2], \tag{A2}$$

respectively. The values calculated from the 20-term Hylleraas wave function are presented in Table III. The values of $F(K)$ should represent a substantial improvement over earlier data from an Eckart wave function[35] and a three-term Hylleraas wave function.[36] The incoherent-scattering function does not seem to have been tabulated yet. The data in Table III should be useful for x-ray analyses of alkali and other strongly ionic hydrides.[37]

TABLE III. The values of $F(K)$ and $S_{\text{inc}}(K)$ computed from the 20-term Hylleraas wave function[14] for H^-.

$(\sin\frac{1}{2}\theta)/\lambda$ (Å^{-1})[a]	Ka_0	$F(K)$	$2S_{\text{inc}}(K)$
0.0	0.0	2.000	0.0
0.025	0.166 24	1.901	0.1781
0.050	0.332 48	1.664	0.5525
0.075	0.498 73	1.393	0.9035
0.100	0.664 97	1.147	1.172
0.125	0.831 21	0.9415	1.376
0.150	0.997 46	0.7730	1.535
0.175	1.1637	0.6362	1.657
0.200	1.3299	0.5252	1.750
0.250	1.6624	0.3618	1.870
0.300	1.9949	0.2527	1.932
0.350	2.3274	0.1791	1.964
0.400	2.6599	0.1288	1.981
0.450	2.9924	0.094 06	1.989
0.500	3.3248	0.069 72	1.994
0.550	3.6573	0.052 44	1.996
0.600	3.9898	0.040 00	1.998
0.650	4.3223	0.030 92	1.999
0.700	4.6548	0.024 20	1.999
0.750	4.9873	0.019 16	1.999
0.800	5.3198	0.015 34	2.000
0.850	5.6522	0.012 40	2.000
0.900	5.9847	0.010 13	2.000
0.950	6.3172	0.008 337	2.000
1.000	6.6497	0.006 921	2.000
1.100	7.3147	0.004 875	2.000
1.200	7.9796	0.003 525	2.000
1.300	8.6446	0.002 608	2.000
1.400	9.3096	0.001 968	2.000
1.500	9.9746	0.001 512	2.000

[a] The variable $(\sin\frac{1}{2}\theta)/\lambda=K/4\pi$, where $\frac{1}{2}\theta$ is the Bragg angle and λ the wavelength, is commonly used in x-ray physics.

We can find an indication of the accuracy of our data by comparing them with those calculated from less accurate wave functions. The values of $F(K)$ and $S_{\text{inc}}(K)$ calculated from the 11-term wave function are in very close agreement with those given in Table III, supporting our earlier statement that the 11-term wave function is practically as good as the 20-term wave function. We estimate that our $F(K)$ is accurate to 3% or better, $F(K)$ for small Ka_0 being likely to be less accurate. The values of $S_{\text{inc}}(K)$ are sensitive to the wave function, and may be in error by 5 to 10% for $Ka_0 \lesssim 0.5$. For $Ka_0 \gtrsim 0.5$, however, $S_{\text{inc}}(K)$ is less sensitive to the wave function, and the expected accuracy is 5% or better.

APPENDIX II. DERIVATION OF EQ. (11)

We shall hereafter use Hartree atomic units. Consider a one-electron system with the Hamiltonian $H=-\frac{1}{2}\Delta+V(r)$. Let u_0 and u_s be the wave functions for the ground state and the excited state s with eigenenergies W_0 and W_s, respectively. The solution $F^{(m)}(\vec{r})(m=1,2,\ldots)$ of a set of equations.

$$\Delta F^{(m)}+2\vec{\nabla}u_0/u_0\cdot\vec{\nabla}F^{(m)}=-2F^{(m-1)},$$

$$F^{(0)}\equiv z, \tag{A3}$$

where z is a Cartesian component of $\vec{r}$, satisfies

$$(s|z|0)(W_s-W_0)^{-m}=(s|F^{(m)}|0) \tag{A4}$$

for every s and m. This lemma, due to Dalgarno and others,[38–40] is readily established by taking matrix elements of

$$HF^{(m)}-F^{(m)}H=-\tfrac{1}{2}[\Delta F^{(m)}+2\vec{\nabla}F^{(m)}\cdot\vec{\nabla}].$$

Equation (A4) permits evaluation of $S(-m)$ $(m\geq 0)$, the moment of the distribution of the oscillator strengths $f_s=2(W_s-W_0)|(s|z|0)|^2$, in the form

$$S(-m)=\sum_{s\neq 0}[2(W_s-W_0)]^{-m}f_s=2^{-m+1}\times\langle zF^{(m-1)}(\vec{r})\rangle, \tag{A5}$$

where $\langle\;\rangle$ denotes a ground-state expectation value, and $\sum_{s\neq 0}$ includes summation over continua. This method has been applied to atomic hydrogen, for which $S(-m)$ up to $m=10$ have been evaluated.[39,41]

We apply the method to the Ohmura model for H⁻, in which case $\sum_{s\neq 0}$ actually means integration over continua only, $S(-m)$ of Eq. (A5) thus being equivalent to that of Eq. (7). Inserting the explicit form of u_0 [Eq. (9)] into Eq. (A3) and putting

$$F^{(m)}(\vec{r}) = z\phi^{(m)}(\rho)/\gamma^{2m} \tag{A6}$$

with $\rho = \gamma r$, we see that $\phi^{(m)}(\rho)$ should satisfy

$$\left[\frac{d^2}{d\rho^2} + \frac{4}{\rho}\frac{d}{d\rho} - 2\left(1+\frac{1}{\rho}\right)\left(\frac{d}{d\rho}+\frac{1}{\rho}\right)\right]\phi^{(m)} = -2\phi^{(m-1)} \tag{A7}$$

with $\phi^{(0)} \equiv 1$.

The solution $\phi^{(m)}(\rho)(m = 1, 2, \ldots)$ can be found in the form

$$\phi^{(m)}(\rho) = \sum_{k=0}^{m} a_k^{(m)} \rho^k , \tag{A8}$$

where $a_k^{(m)}$ are constants. Substitution of Eq. (A8) into Eq. (A7) yields the recurrence relations

$$a_m^{(m)} = a_{m-1}^{(m-1)}/(m+1),$$

$$a_k^{(m)} = [k(k+3)a_{k+1}^{(m)} + 2a_{k-1}^{(m-1)}]/[2(k+1)],$$

$$(k = 1, 2, \ldots, m-1) \tag{A9}$$

with $a_0^{(m)} = \delta_{m0}$.

Equations (A9) determine $a_k^{(m)}$ as

$$a_{m-l}^{(m)} = \frac{(m-l)_{2l}}{(m+1)!\,l!\,2^l} , \quad (l = 0, 1, \ldots, m-1), \tag{A10}$$

where $(\alpha)_n = \alpha(\alpha+1)\ldots(\alpha+n-1) = \Gamma(\alpha+n)/\Gamma(\alpha)$.

Use of Eqs. (A6), (A8), and (A10) now gives $F^{(m)}(\vec{r})$, and thence $S(-m)$ of Eq. (A5):

$$S(-m) = (2\gamma^2)^{-m+1}\left\langle z^2 \sum_{k=0}^{m-1} a_k^{(m-1)} (\gamma r)^k \right\rangle$$

$$= \frac{A^2}{3 \times 2^{m-1}\gamma^{2m}} \sum_{k=0}^{m-1} a_k^{(m-1)} (k+2)!/2^{k+2} . \tag{A11}$$

For $m = 1$, Eq. (A11) readily confirms Eq. (11). For $m \geqq 2$, we insert Eq. (A10) into Eq. (A11) to obtain

$$S(-m) = \frac{A^2}{2^{2m-1} m(m-1)\gamma^{2m}} \sum_{l=0}^{m-2} \frac{(m-1)_l}{3!\,l!} \times (m+1-l)(m-l)(m-1-l) .$$

The summation in the above equation can easily be performed by repeated use of an elementary formula

$$\sum_{k=0}^{n} (\alpha)_k/k! = (\alpha+1)_n/n! ,$$

and the result leads to Eq. (11) with $\mu = -m$.

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Critical Assessment of the Polarized-Orbital Method in Atomic Scattering*

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The method of polarized orbitals used in calculating electron-atom scattering amplitudes has two obvious flaws: the wave function is discontinuous, and the method is not variationally based. These are corrected in a somewhat arbitrary manner, and it is found that the results then depend upon a parameter of the theory sufficiently strongly that there are serious doubts about the predictive nature of the theory.

I. INTRODUCTION

Techniques for calculating the scattering amplitude of an electron by an atom may be divided into three categories, predictive, checkable, or phenomenological. By the first we mean a no-parameter theory which purports to describe the situation. For example, the "optical potential" method was such an attempt.[1] It contains the static-exchange approximation with the variational inclusion of the long-range polarization effects. A prescription for the continuation of the polarization potential to small r was given with the expectation that the Pauli principle would make the results less dependent on the details of the cutoff. This expectation was borne out but not sufficiently to give quantitative agreement. That is, the cutoff parameter for the polarization potential still had to be chosen to give a fit with experiments. This then made the theory of the third type, the phenomenological. The close coupling method,[2] and its offshoots,[3] are examples of our second category, the checkable ones, as are other variationally based calculations.[4] By this we mean that when a basis is chosen for a variational calculation, the reliability of the results can usually be assessed by a comparison with an expanded basis.[5]

Theories of the first kind are the most ambitious and the most valuable. The method of polarized orbitals[6] (p.o.) has been interpreted as such a theory and is becoming more widely relied upon as such.[7] It is the object of this note to investigate the reliability of this method by correcting its obvious flaws and assessing its accuracy. In order to do this, we have presented (in the next section) a new ansatz for the trial form of the wave function. We emphasize here that this is not presented as a new and desirable way to calculate electron scattering but merely as a generalization of the p.o. method designed to assess its accuracy. Also in the next section, we discuss the simple case of s-wave electron-hydrogen singlet scattering. The singlet is chosen in that it is a more stringent test of the theory than is the triplet.

II. FORMAL DEVELOPMENT AND RESULTS

The p.o. method is designed to give an approximate solution for the scattering described by the Schrodinger equation

$$(E-H)\underline{\psi}=0 \tag{1}$$

The method is based on an assumed form for a scattering wave function, which for singlet s-wave