

Effective dipole-oscillator-strength distribution and its applications

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A new procedure for the construction of effective dipole-oscillator-strength distributions is proposed. The effective distributions satisfy not only the usual sum rules, but also have the correct asymptotic behavior and satisfy a "modified" oscillator-strength sum rule. The distributions may be used to evaluate logarithmic mean excitation energies. The application of the effective distributions toward the calculation of the high-energy photoionization cross section is also discussed. Calculations on atomic hydrogen have been performed which indicate the technique is an efficient method for the computation of the excitation energies. Finally, the technique is applied to atomic helium and the negative hydrogen ion.

I. INTRODUCTION

Various attempts have been made in the past to utilize information from sum rules and knowledge of the asymptotic form of the oscillator-strength density for calculations of atomic and molecular properties. Dalgarno and Lynn¹ modified available theoretical values of oscillator strengths of atomic helium to satisfy sum rules, while assuming a functional form for the oscillator-strength density with a reasonable asymptotic behavior. They then employed the new values to evaluate various properties of helium arising from second-order perturbation theory. Dalgarno and Stewart² followed a similar procedure to calculate the Lamb shift of helium, with improved values of oscillator strengths and the correct coefficient of the first asymptotic term of the oscillator-strength density. Garcia³ has suggested an approximate analytic representation of the oscillator-strength moment, $S(k)$, which can be fitted to a set of values (at $k=2, 1, 0, -1, -2, -4, -6$) known from sum rules and experiment. Garcia's representation of $S(k)$ is consistent with the asymptotic form of the oscillator-strength density and can be used to obtain estimates of the Bethe logarithm required for the evaluation of the Lamb shift.

The present work describes the construction of an effective oscillator-strength distribution which satisfies not only the usual sum rules, but also has the correct asymptotic behavior and satisfies the "modified" oscillator-strength sum rule described in previous work.⁴ The functional form for the effective distribution consists of discrete states plus a continuous density extending from infinity down to some cutoff value of the energy. The constants required to specify the effective distribution are obtained by solving a system of nonlinear algebraic equations. In previous work,⁵ which described the solution of a similar system of equations, a rather remarkable simplification reduced the problem to one of finding the roots of a polynomial. No such simplifications occur here, and the approach used to solve the equations is the multidimensional generalization of the Newton-Raphson method. Once the effective distribution has been obtained, it is a simple matter to obtain estimates for the logarithmic

mean excitation energies and the photoionization cross section.

Calculations using the effective distributions are then performed on atomic hydrogen, atomic helium, and the negative hydrogen ion. For atomic hydrogen, the results obtained from the effective distribution are found to be in very good agreement with exact results. For atomic helium and the negative hydrogen ion, the moments $S(k)$ of the oscillator-strength distribution, needed for implementing the method, have been taken from the literature. However, accurate values of $S_f(3)$ (the "finite" part of the third moment of the oscillator-strength distribution), also needed, have not previously been available. In order to obtain $S_f(3)$ to the required accuracy, calculations have been performed using a 162-term He ground state and a 162-term H^- ground state, both containing Fock terms in the wave function. The resulting calculations of the logarithmic mean excitation energies $L(k)$ appear to be the most accurate to date of $L(1)$, $L(0)$, and $L(-1)$ for atomic helium and of $L(2)$, $L(1)$, $L(0)$, and $L(-1)$ for the negative hydrogen ion.

II. THE EFFECTIVE DISTRIBUTION AND ITS MOMENTS

The effective oscillator-strength distribution is assumed to consist of a set of M discrete states and a continuous density. The m th discrete state is completely determined by specifying the oscillator strength f'_m and the associated energy difference (with the ground state) ω'_m . The effective oscillator-strength density is of the form

$$\frac{df'}{d\epsilon} = \alpha(\epsilon - \epsilon_0)^{-7/2} + \beta(\epsilon - \epsilon_0)^{-4} + \gamma(\epsilon - \epsilon_0)^{-9/2} \quad (1)$$

(where ϵ_0 is the ground-state energy), and extends over the energy from infinity down to some cutoff energy $\epsilon=b$. Some explanation is necessary for the particular form for the expansion taken in Eq. (1). The above expansion for $df'/d\epsilon$ is certainly not unique and any expansion which leads to the correct asymptotic behavior is allowable. For instance, the replacement of the variable $\epsilon - \epsilon_0$ by $\epsilon - C$, where C is any real constant, is also a possible expansion.

The two obvious choices for C would seem to be 0 or ϵ_0 . C was not chosen to be zero because that would indicate an inherent divergence at $\epsilon=0$ which is physically unacceptable. Furthermore, from a practical point of view, the choice $C=\epsilon_0$ leads to the simplest possible integrals for the technique described in this paper. From a more sophisticated point of view, the work of Dillon and Inokuti⁶ shows that the expansion of the "reduced" oscillator-strength density may be written as a power series in the variable $g=\epsilon/(\epsilon-\epsilon_0)$. They also find that polynomial approximants in the variable g provide good representations of not only the reduced density, but also of the original density. Noting that $g=1+\epsilon_0(\epsilon-\epsilon_0)^{-1}$ shows that if a function can be written as a power series in g , then it can also be written as a power series in $(\epsilon-\epsilon_0)^{-1}$. This would seem to indicate some additional justification for the use of $(\epsilon-\epsilon_0)^{-1}$ as an expansion variable; however, the presence of the half-powers of $(\epsilon-\epsilon_0)^{-1}$ in Eq. (1) makes this argument far from being rigorous.

Clearly the k th moment of the above distribution (with respect to the energy difference with the ground-state energy) is given by

$$S'(k) = \sum_{n=1}^M f'_n (\omega'_n)^k + \frac{\alpha}{\frac{5}{2}-k} (b-\epsilon_0)^{k-5/2} + \frac{\beta}{3-k} (b-\epsilon_0)^{k-3} + \frac{\gamma}{\frac{7}{2}-k} (b-\epsilon_0)^{k-7/2}. \quad (2)$$

$$\tilde{S}(k,b) = \sum_n f_{0n} \omega_{0n}^k + \int_{\epsilon_I}^{\infty} \left[\frac{df}{d\epsilon} - \Theta(\epsilon-b) [\alpha(\epsilon-\epsilon_0)^{-7/2} + \beta(\epsilon-\epsilon_0)^{-4}] \right] (\epsilon-\epsilon_0)^k d\epsilon, \quad (6)$$

where f_{0n} and ω_{0n} are the oscillator strength and energy difference between the ground state $|0\rangle$ and bound state $|n\rangle$. It is easily verified that $\tilde{S}(k,b)$ is related to $S(k)$, the k th moment of the oscillator-strength distribution, through the equation

$$\tilde{S}(k,b) = S(k) - \frac{\alpha}{\frac{5}{2}-k} (b-\epsilon_0)^{k-5/2} - \frac{\beta}{3-k} (b-\epsilon_0)^{k-3}. \quad (7)$$

The basic approach to be followed here is to fit the $S'(k)$ [defined in Eq. (2)] to a set of known $S(k)$. However, it is known from the derivation given in Ref. 4 that the third moment of the "modified" distribution is also known. The procedure described here allows the effective distribution to satisfy the usual moments known from sum rules and, in addition, allows the "modified" effective distribution to satisfy the value of the third moment of the actual "modified" oscillator-strength distribution. Note that $S(k)$ is infinite for $k=3$; however, $\tilde{S}(3,b)$ is well defined, and from the results presented in Ref. 4 it is known that

$$\tilde{S}(3,b) = S_f(3) + 2\alpha(b-\epsilon_0)^{1/2} + \beta \ln(b-\epsilon_0), \quad (8)$$

where $S_f(3)$, the "finite" part of $S(3)$, is given for atoms by

For atoms, the α and β are chosen to be

$$\alpha = \frac{2}{3} \frac{Z^2 \sqrt{2}}{\pi} N \rho(0) \quad (3)$$

and

$$\beta = -\frac{2}{3} Z^3 N \rho(0), \quad (4)$$

where Z is the nuclear charge, N is the number of electrons, and $\rho(0)$ is the one-electron density at the nucleus. For molecules, the corresponding expressions listed in Ref. 4 must be used. With this choice of α and β , the effective oscillator-strength density correctly assumes the first two asymptotic terms of the actual oscillator-strength density, as shown in Ref. 4.

For the continuum oscillator-strength density $df/d\epsilon$, which lies above the first ionization energy ϵ_I , it shall prove necessary to introduce a modified oscillator-strength density of the form

$$\tilde{\frac{df}{d\epsilon}} = \frac{df}{d\epsilon} - \Theta(\epsilon-b) [\alpha(\epsilon-\epsilon_0)^{-7/2} + \beta(\epsilon-\epsilon_0)^{-4}], \quad (5)$$

where Θ is the unit step function and b is some cutoff energy lying between ϵ_I and infinity. Then $\tilde{S}(k,b)$, the k th moment of the modified oscillator-strength distribution consisting of the (unmodified) discrete states plus the modified density above ϵ_I , is given by

$$S_f(3) = \frac{4}{3} Z^3 N \rho(0) \left(\frac{1}{2} \ln 2 - \frac{1}{2} - C_{EM} \right) + \frac{2}{3} Z^2 \left[\sum_{\substack{i,j=1 \\ i \neq j}}^N \left\langle \psi_0 \left| \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_i^3 r_j^3} \right| \psi_0 \right\rangle - N \int_0^{\infty} \ln r \frac{d^2 \rho}{dr^2} dr \right], \quad (9)$$

with $C_{EM}=0.5772\dots$, the Euler-Mascheroni constant. For molecules $S_f(3)$ is given by the generalization easily obtained from the results presented in Ref. 4.

The effective oscillator-strength distribution described above contains the unknown parameters γ , b , and f'_n and ω'_n for $n=1,2,\dots,M$. These $2M+2$ unknown constants shall be determined by requiring that $2M+2$ of the moments of the effective distribution are equal to those of the actual oscillator-strength distribution (known from sum rules, experiment, variational calculations, etc.). Of the resulting $2M+2$ equations, one of these equates the third moment of the modified oscillator-strength distribution to the third moment of the corresponding modified effective distribution. More precisely, it shall be required that the effective distribution satisfy

$$\tilde{S}(k,b) = \sum_{n=1}^M f'_n(\omega'_n)^k + \frac{\gamma}{\frac{7}{2}-k} (b-\epsilon_0)^{k-7/2} \quad (10)$$

for $k=3,2,1, \dots, -2M+2$.

III. THE DETERMINATION OF THE SOLUTION OF THE SYSTEM OF EQUATIONS

The system of nonlinear algebraic equations described in the preceding section is considerably more difficult to solve than that encountered in Ref. 5. The questions concerning the existence and uniqueness of the solution are not easily answered and the application of algebra is not capable of significantly reducing the system (for the case of M an arbitrary integer) into a tractable form. An operational procedure, proven successful for solving the system for all cases encountered in this paper, shall be described, which is based on the fixed-point iteration technique. Fixed-point methods typically require a reasonably accurate initial guess to the solution, in order to achieve convergence. The approach taken here to obtain the initial guess relies on the solution to the equations described in Ref. 5 and also requires the solution to the system described in the preceding section for the special case of $M=1$.

For the case of $M=1$, the system for which a solution is desired is given by

$$\begin{aligned} \tilde{S}(3,b) &= f'_1(\omega'_1)^3 + 2\gamma(b-\epsilon_0)^{-1/2}, \\ \tilde{S}(2,b) &= f'_1(\omega'_1)^2 + \frac{2}{3}\gamma(b-\epsilon_0)^{-3/2}, \\ \tilde{S}(1,b) &= f'_1\omega'_1 + \frac{2}{5}\gamma(b-\epsilon_0)^{-5/2}, \\ \tilde{S}(0,b) &= f'_1 + \frac{2}{7}\gamma(b-\epsilon_0)^{-7/2}. \end{aligned} \quad (11)$$

The system is first simplified by replacing the b appearing on the left-hand side [in the $\tilde{S}(k,b)$ terms] by an initial guess, b' . The solution of this system can be achieved by algebraic manipulation of the equations into a single polynomial equation in the variable b . Choosing the highest real root of this polynomial has been found to lead to physically reasonable effective oscillator-strength distributions. Then, an iteration procedure (bisection) is used to determine the initial guess b' which coincides with this highest root for b . f'_1 , ω'_1 , and γ are easily determined once b is known. More details and justification are contained in Ref. 7.

Having described the procedure for solving the $M=1$ case of the system of equations developed in the preceding section, it is now possible to obtain a fairly accurate initial estimate of the solution for the general case of M equal to some arbitrary integer. The first step is to set up the system of equations given by

$$\tilde{S}(k,b') = \sum_{n=1}^{M+1} f'_n(\omega'_n)^k \quad (12)$$

for $k=3,2,1, \dots, -2M+2$, where some reasonable value b' has been assumed for b . The system given by Eq. (12) can be solved by the techniques of Ref. 5, leading to a collection of effective states consisting of f'_m and ω'_m for

$m=1,2,3, \dots, M+1$. For the following, it is assumed that the states have been labeled such that the effective energy difference ω'_m monotonically increases as a function of the index m . Then the two highest-energy effective states (f'_M, ω'_M and f'_{M+1}, ω'_{M+1}) are to be replaced by an effective state and an effective density using the procedure described previously to solve the system given by Eq. (11). This replacement is accomplished by using the two highest-energy effective states to determine values for the moments $\tilde{S}(3,b')$, $\tilde{S}(2,b')$, $\tilde{S}(1,b')$, and $\tilde{S}(0,b')$ appearing in Eq. (11), according to

$$\begin{aligned} \tilde{S}(3,b') &= f'_M(\omega'_M)^3 + f'_{M+1}(\omega'_{M+1})^3, \\ \tilde{S}(2,b') &= f'_M(\omega'_M)^2 + f'_{M+1}(\omega'_{M+1})^2, \\ \tilde{S}(1,b') &= f'_M\omega'_M + f'_{M+1}\omega'_{M+1}, \\ \tilde{S}(0,b') &= f'_M + f'_{M+1}. \end{aligned} \quad (13)$$

Equation (11) is then solved in the usual manner to obtain the new effective state and effective density which replaces the effective states f'_M, ω'_M and f'_{M+1}, ω'_{M+1} . As before, the iteration procedure is used to force b' to coincide with b .

The claim that the above procedure provides a good estimate for the actual desired solution is easily justified. The effective distribution which has been constructed is of the form specified in the preceding section, i.e., with M discrete states plus the continuous density. This distribution satisfies Eq. (10) exactly for $k=0,1,2$, and 3. The remaining equations for $k=-1, -2, \dots, -2M+2$ are more sensitive to the behavior of the low-lying discrete states, so the conversion of the two highest discrete states into a discrete state plus a continuous density should not cause these equations to be violated too badly. Hence the above procedure should provide an adequate initial guess for the fixed-point iteration technique described below. In practice this method has proved successful for calculations on various test cases.

After dealing with the subtle problem of obtaining the initial guess, the task of implementing a fixed-point iteration procedure on the system given in Eq. (10) is quite straightforward. The specific technique to be used is the well-known multidimensional generalization of the Newton-Raphson method.⁸ This method finds the values of x_1, x_2, \dots, x_N which satisfy the system of equations

$$\phi_i(x_1, x_2, \dots, x_N) = 0 \quad (14)$$

for $i=1,2, \dots, N$. The solution is obtained by iterating the transformation

$$\mathbf{x}' = \mathbf{x} - \underline{J}^{-1}(\mathbf{x})\phi(\mathbf{x}) \quad (15)$$

until convergence is achieved, where $\underline{J}(\mathbf{x})$ is the Jacobian matrix,

$$\underline{J}(\mathbf{x}) = \begin{pmatrix} \frac{\partial \phi_1}{\partial x_1} & \frac{\partial \phi_1}{\partial x_2} & \dots & \frac{\partial \phi_1}{\partial x_N} \\ \frac{\partial \phi_2}{\partial x_1} & \frac{\partial \phi_2}{\partial x_2} & \dots & \dots \\ \vdots & \vdots & & \vdots \\ \frac{\partial \phi_N}{\partial x_1} & \dots & \dots & \frac{\partial \phi_N}{\partial x_N} \end{pmatrix} \quad (16)$$

and \mathbf{x} , \mathbf{x}' , and ϕ are column vectors. Technical details are contained in Ref. 7.

IV. RESULTS FROM THE EFFECTIVE DISTRIBUTIONS FOR ATOMIC HYDROGEN

Effective oscillator-strength distributions have been constructed for atomic hydrogen using the procedure described in the preceding section for the $M=1, 2, 3$, and 4 cases. In addition, effective oscillator-strength distributions can be constructed which include some of the lowest excited p states explicitly,⁷ but these results are not presented here because they do not lead to particularly dramatic improvement in the quantities calculated.

The moments and asymptotic coefficients are easily obtained for atomic hydrogen,^{4,5} but will be listed here for

$$L(k) = \sum_{n=1}^M f_n'(\omega_n')^k \ln \omega_n' + \frac{\alpha}{\frac{5}{2}-k} (b-\epsilon_0)^{k-5/2} \ln(b-\epsilon_0) + \frac{\alpha}{(\frac{5}{2}-k)^2} (b-\epsilon_0)^{k-5/2} \\ + \frac{\beta}{3-k} (b-\epsilon_0)^{k-3} \ln(b-\epsilon_0) + \frac{\beta}{(3-k)^2} (b-\epsilon_0)^{k-3} + \frac{\gamma}{\frac{7}{2}-k} (b-\epsilon_0)^{k-7/2} \ln(b-\epsilon_0) + \frac{\gamma}{(\frac{7}{2}-k)^2} (b-\epsilon_0)^{k-7/2}. \quad (18)$$

Values for $L(2)$, $L(1)$, $L(0)$, and $L(-1)$ are listed in Table I and compared with exact results. For purposes of comparison, in Table II are presented the logarithmic mean excitation energies obtained using the standard moment-theory technique, described in Ref. 5. In the standard moment-theory approach, effective distributions are constructed from either (i) an even number of moments [e.g., $S(2)-S(1)$, $S(2)-S(-1)$, $S(2)-S(-3)$, $S(2)-S(-5)$], or (ii) an odd number of moments [e.g., $S(2)-S(0)$, $S(2)-S(-2)$, $S(2)-S(-4)$, $S(2)-S(-6)$] along with the lowest dipole transition energy. Examining the $M=4$ effective distribution results listed in Table I, which are the most accurate calculations performed here, it seems most reasonable to compare these with the $S(2)-S(-6)$ standard moment-theory results listed in Table II. Note that the $M=4$ distribution in Table I is constructed from $S_f(3), S(2), S(1), \dots, S(-6)$ [along with the asymptotic coefficients α and β , which are known once $S(2)$ is known, for atoms], while the $S(2)-S(-6)$ distribution is constructed from $S(2), S(1), \dots, S(-6)$ and the lowest dipole transition energy, which for atomic hydrogen is 0.375 a.u. Comparing the $M=4$ results of Table I with the $S(2)-S(-6)$ results of Table II, it is seen that requiring the effective distribution to satisfy $S_f(3)$ and the

completeness. The moments used are

$$S_f(3) = 8 \ln 2 - \frac{8}{3}, \quad S(2) = \frac{4}{3}, \quad S(1) = \frac{2}{3}, \\ S(0) = 1, \quad S(-1) = 2, \quad S(-2) = \frac{9}{2}, \quad S(-3) = \frac{43}{4}, \\ S(-4) = \frac{319}{12}, \quad S(-5) = \frac{9673}{144}, \quad S(-6) = \frac{297541}{1728}.$$

Note that atomic units are used throughout this work unless specified otherwise. The coefficients of the first two asymptotic terms of the oscillator-strength density are $\alpha = 8\sqrt{2}/(3\pi)$ and $\beta = -\frac{8}{3}$.

The logarithmic mean excitation energies $L(k)$ are defined⁵ by

$$L(k) = \sum_n f_{0n}(\omega_{0n})^k \ln \omega_{0n}, \quad (17)$$

where n ranges over all dipole allowed states $|n\rangle$, both discrete and continuous. For $k = -1, 0, 1$ these $L(k)$ are required for the evaluation of properties which characterize the inelastic scattering of fast charged particles with atoms and molecules. $L(2)$ is needed to evaluate the Lamb shift. The effective distributions have been used to obtain estimates of the logarithmic mean excitation energies by evaluating the $L(k)$ associated with the effective distributions, i.e.,

correct asymptotic behavior has led to significantly better results than those obtained from the standard moment-theory technique. The $M=4$ results obtained for $L(0)$ and $L(2)$ are also significantly better than those obtained using Garcia's interpolation scheme [note Garcia considered only $L(0)$ and $L(2)$]. The effective distributions constructed here may also be of some interest. These are listed in Table III.

V. THE HIGH-ENERGY PHOTOIONIZATION CROSS SECTION

The expansion given in Eq. (1) may be useful for estimating the photoionization cross section at high ener-

TABLE I. Values of logarithmic mean excitation energies (in rydbergs) obtained from effective distributions for atomic hydrogen.

M	$L(-1)$	$L(0)$	$L(1)$	$L(2)$
1	0.153 83	0.151 91	0.7128	16.109
2	-0.074 93	0.099 07	0.7545	15.978
3	-0.073 34	0.097 24	0.7595	15.942
4	-0.073 26	0.097 04	0.7606	15.929
Exact ^a	-0.073 25	0.096 98	0.7612	15.915

^aReference 18.

TABLE II. Values of logarithmic mean excitation energies (in rydbergs) obtained from standard moment theory for atomic hydrogen.

Moments included	$L(-1)$	$L(0)$	$L(1)$	$L(2)$
$S(2)-S(1)$	0.115 52	0.462 10	1.848	7.39
$S(2)-S(0)$	-0.326 49	-0.087 40	1.104	9.52
$S(2)-S(-1)$	-0.025 75	0.054 86	0.933	10.61
$S(2)-S(-2)$	-0.068 12	0.085 74	0.846	11.59
$S(2)-S(-3)$	-0.071 58	0.091 34	0.820	12.03
$S(2)-S(-4)$	-0.072 85	0.094 78	0.796	12.60
$S(2)-S(-5)$	-0.073 05	0.095 57	0.788	12.85
$S(2)-S(-6)$	-0.073 18	0.096 31	0.779	13.23

gies. The total photoionization cross section σ , in the dipole approximation, is related to the oscillator-strength density $df/d\epsilon$ (when ϵ is given in atomic units) by⁹

$$\sigma = 2\pi^2 \alpha a_0^2 \frac{df}{d\epsilon}, \quad (19)$$

where $\alpha = e^2/\hbar c \approx \frac{1}{137}$ is the fine-structure constant and $a_0 = \hbar^2/me^2$ is the Bohr radius.

Using the best value of γ obtained from Table III leads to the approximate expansion

$$\frac{df'}{d\epsilon} = \frac{8\sqrt{2}}{3\pi} (\epsilon - \epsilon_0)^{-3.5} - \frac{8}{3} (\epsilon - \epsilon_0)^{-4} + 3.46 (\epsilon - \epsilon_0)^{-4.5}. \quad (20)$$

Comparing this with the exact expression⁴ for $df/d\epsilon$, one finds that Eq. (20) leads to a result approximately 9% too high at $\epsilon - \epsilon_0 = 10$ a.u. and to a result approximately 2% too high at 20 a.u. (and, of course, even better at higher energies). The approximate total photoionization cross section associated with Eq. (20) is given by

TABLE III. Effective distributions for atomic hydrogen.

M		
1	$f'_1 = 0.956 57$ $\gamma = 3.07 17$	$\omega'_1 = 0.539 56$ $b - \epsilon_0 = 2.1186$
2	$f'_1 = 0.711 86$ $f'_2 = 0.271 25$ $\gamma = 3.25 15$	$\omega'_1 = 0.408 78$ $\omega'_2 = 1.0653$ $b - \epsilon_0 = 3.0560$
3	$f'_1 = 0.530 47$ $f'_2 = 0.362 28$ $f'_3 = 0.099 038$ $\gamma = 3.374 8$	$\omega'_1 = 0.383 45$ $\omega'_2 = 0.649 55$ $\omega'_3 = 1.7247$ $b - \epsilon_0 = 4.0812$
4	$f'_1 = 0.455 42$ $f'_2 = 0.305 93$ $f'_3 = 0.190 51$ $f'_4 = 0.043 580$ $\gamma = 3.464 7$	$\omega'_1 = 0.377 11$ $\omega'_2 = 0.531 29$ $\omega'_3 = 0.960 02$ $\omega'_4 = 2.4963$ $b - \epsilon_0 = 5.1958$

TABLE IV. He ground-state expectation values as a function of basis size.

Number of terms included	Energy	I_2	I_3
89	-2.903 724 376 161	-1.367 00	-180.941
101	-2.903 724 376 985	-1.366 95	-180.935
117	-2.903 724 377 018	-1.366 94	-180.940
137	-2.903 724 377 023	-1.366 93	-180.936
162	-2.903 724 377 025	-1.366 93	-180.937
Best estimate	-2.903 724 377 034 ^a	-1.366 93	-180.937

^aReference 19.

$$\sigma' = 2\pi^2 \alpha a_0^2 \left[\frac{8\sqrt{2}}{3\pi} (\epsilon - \epsilon_0)^{-3.5} - \frac{8}{3} (\epsilon - \epsilon_0)^{-4} + 3.46 (\epsilon - \epsilon_0)^{-4.5} \right], \quad (21)$$

and the corresponding dipole approximation to the differential cross section is given by

$$\frac{d\sigma'}{d\Omega} = \frac{3\pi}{4} \alpha a_0^2 \sin^2 \theta \left[\frac{8\sqrt{2}}{3\pi} (\epsilon - \epsilon_0)^{-3.5} - \frac{8}{3} (\epsilon - \epsilon_0)^{-4} + 3.46 (\epsilon - \epsilon_0)^{-4.5} \right], \quad (22)$$

where the differential cross section has been averaged over both helicity states of the incoming photons and θ is measured from the direction of the propagation of the light.¹⁰

The dipole approximation is certain to hold⁹ only for energies such that $\epsilon - \epsilon_0 \ll \epsilon_0/\alpha \approx 68.5$ a.u. Beyond 20 a.u. it might be argued that the dipole approximation is being violated. However, for the case of atomic hydrogen it can be shown¹⁰ that, asymptotically, the differential cross section (including all multipoles) is given by

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= 2\sqrt{2} \alpha a_0^2 (\epsilon - \epsilon_0)^{-3.5} \sin^2 \theta \left[1 + 4 \frac{\nu}{c} \cos \theta \right] \\ &= 2\sqrt{2} \alpha a_0^2 (\epsilon - \epsilon_0)^{-3.5} \\ &\quad \times \sin^2 \theta \left[1 + 4\alpha \left(\frac{\epsilon - \epsilon_0}{\epsilon_0} \right)^{1/2} \cos \theta \right], \end{aligned} \quad (23)$$

TABLE V. H⁻ ground-state expectation values as a function of basis size.

Number of terms included	Energy	I_2	I_3
89	-0.527 750 699	-0.055 84	-5.355
101	-0.527 750 929	-0.056 06	-5.363
117	-0.527 750 967	-0.056 10	-5.354
137	-0.527 750 989	-0.056 10	-5.347
162	-0.527 751 000	-0.056 09	-5.350
Best estimate	-0.527 751 016 ^a	-0.056 09	-5.349

^aReference 20.

TABLE VI. Asymptotic coefficients and moments from sum rules for He and H⁻.

	He	H ⁻
α	54.6204	1.241 12
β	-242.672	-2.757 08
$S_f(3)$	606.76	3.066
$S(2)$	30.3340	1.378 54
$S(1)$	4.083 73	0.747 508
$S(0)$	2.000 00	2.000 00
$S(-1)$	1.505 00	14.9685

where v is the velocity of the ejected electron. This form for writing the asymptotic expansion is reasonable if $v/c \ll 1$, which is simply the assumption that only the nonrelativistic case is being considered (already required by the fact that the Schrödinger equation rather than the Dirac equation is being used). The expansion in Eq. (23) contains only two leading terms of an expansion which should be in powers of both $(\epsilon - \epsilon_0)^{-1/2}$ and v/c , i.e., terms of the type appearing in Eq. (22) should also be in the expansion. Equation (23), however, indicates the importance of the higher multipoles to the actual expansion. For v/c sufficiently small, Eq. (22) should be a better expansion than Eq. (24). Note that the second term in Eq. (24) is small when $\epsilon - \epsilon_0 \ll \epsilon_0/16\alpha^2 \approx 586.5$ a.u. Therefore, although the dipole requirement that $\epsilon - \epsilon_0 \ll 68.5$ a.u. is sufficient for Eq. (22) to be useful, it is more stringent than necessary. Also note that when Eq. (24) is integrated over all solid angle to obtain the total cross section, the contribution from the second term in the expansion vanishes by virtue of the angular dependence. The next term in v/c will be of order $(v/c)^2$ and presumably will be less important than the first-order term which appeared in the differential cross section. Therefore Eq. (21) should serve as a better approximation to the total cross section than Eq. (22) serves for the differential cross section. Finally, note that the $(v/c)^2$ term can be shown⁹ to be of the same order as relativistic effects, so to proceed beyond this point the Dirac equation must be used. In conclusion, Eqs. (21) and (22) should serve fairly well in the high-energy region and it appears that this behavior should also hold true for other atoms.

VI. THE CALCULATION OF $S_f(3)$ FOR He AND H⁻

In order to construct the effective oscillator-strength distributions for atomic helium and the negative hydrogen ion it is necessary to have accurate values of the usual moments $S(k)$ for $k=2,1,0,-1,\dots$ as well as $S_f(3)$, the "finite" part of the third moment. Note that in Ref. 4 it

TABLE VII. Variational moments used for He and H⁻.

	He	H ⁻
$S(-2)$	1.383 12	206.0959
$S(-3)$	1.414 96	3 771.499
$S(-4)$	1.542 10	80 102.66
$S(-5)$	1.749 87	1 867 814
$S(-6)$	2.040 44	46 472 740

TABLE VIII. Case $M=4$ effective distributions for He and H⁻.

He	
$f'_1=0.4874$	$\omega'_1=0.8060$
$f'_2=0.7506$	$\omega'_2=1.194$
$f'_3=0.6132$	$\omega'_3=2.434$
$f'_4=0.1386$	$\omega'_4=7.213$
$\gamma=640.9$	$b - \epsilon_0=17.45$
H ⁻	
$f'_1=0.074 82$	$\omega'_1=0.035 43$
$f'_2=0.4227$	$\omega'_2=0.060 50$
$f'_3=0.8195$	$\omega'_3=0.1662$
$f'_4=0.6528$	$\omega'_4=0.7027$
$\gamma=3.346$	$b - \epsilon_0=2.498$

TABLE IX. Comparison of values of $L(k)$ for atomic helium.

$L(-1)$	Source
0.6456±0.0015	Moment theory ^a
0.6382±0.0020	Consistent distribution ^b
0.6438	Present work ($M=4$)
0.6440±0.0004	Present work (extrapolated)
$L(0)$	Source
2.256±0.015	Moment theory ^a
2.254	Variational calculation ^c
2.260	Variational calculation ^d
2.240	$S(k)$ fit ^e
2.11	$S(k)$ fit ^f
2.263	$S(k)$ fit ^g
2.361	Experimental ^h
2.223	Experimental ⁱ
2.267	Present work ($M=4$)
2.265±0.003	Present work (extrapolated)
$L(1)$	Source
14.72±0.50	Moment theory ^a
13.76	Variational calculation ^d
14.6	$S(k)$ fit ^f
14.57	Present work ($M=4$)
14.58±0.03	Present work (extrapolated)
$L(2)$	Source
521.7	$S(k)$ fit ^g
530.2	Consistent distribution ^j
530.2±0.5	Variational calculation ^k
530.8	Present work ($M=4$)
530.1±0.7	Present work (extrapolated)

^aReference 21.^bReference 22.^cReference 23.^dReference 24.^eReference 25.^fReference 26.^gReference 3.^hReference 27.ⁱReference 28.^jReference 2.^kReference 11.

is shown that the coefficients α and β of the first two asymptotic terms of the oscillator-strength density may be obtained from $S(2)$. Sufficiently accurate values of the $S(k)$ have been found in the literature; however, it has been necessary to perform calculations utilizing highly accurate He and H^- wave functions to obtain $S_f(3)$ to the required accuracy.

A calculation from which $S_f(3)$ may be obtained has been performed previously for He by Schwartz,¹¹ but this has been found to be inadequate for the present needs. Note that $S_f(3)$ may be written in terms of what Schwartz calls "C" through the relation

$$S_f(3) = \frac{2}{3} Z^2 N \rho(0) C. \quad (25)$$

Schwartz performed a calculation using an 18-term Kinoshita wave function and obtained $C=5.18$ for atomic helium. Using Pekeris's result,¹² $N\rho(0)=45.501$, leads to $S_f(3)=629$ for He, in substantial disagreement with the value obtained in the present work.

The wave function used for the present calculation is a modified version of a Fock-type wave function due to C. W. Scherr and E. J. Shipsey (unpublished). The wave function is of the form

$$\psi = e^{-\lambda(r_1+r_2)/2} P(r_1, r_2, r_{12}), \quad (26)$$

where

$$P = \sum_{\substack{p,q,l, \\ i,j}} A(p,q,l,i,j) r_1^p r_2^q r_{12}^l (r_1^2 + r_2^2)^{i/2} [\ln(r_1^2 + r_2^2)]^j \quad (27)$$

as specified by Fock,¹³ where r_1 , r_2 , and r_{12} are the Hylleraas variables. The permutational symmetry of the ground state has been insured by requiring $A(p,q,l,i,j) = A(q,p,l,i,j)$. The standard Rayleigh-Ritz procedure¹⁴ has been employed to determine the values of $A(p,q,l,i,j)$ and λ for which the expectation value of the energy is minimized. The inclusion of the nonconventional half-power and logarithmic terms is necessary in order for the wave function to assume the correct analytic form when both electrons are near the nucleus. This type of wave function appears to be especially well suited for the present calculation since the expectation values necessary for the evaluation of $S_f(3)$ are clearly very sensitive to the behavior of the wave function near the nucleus. From Eq. (9), $S_f(3)$ may be written as

$$S_f(3) = I_1 + \frac{2}{3} Z^2 I_2 - \frac{2}{3} Z^2 N I_3, \quad (28)$$

where

$$I_1 = \frac{4}{3} Z^2 N \rho(0) \left[\frac{1}{2} \ln 2 - \frac{1}{2} - C_{EM} \right], \quad (29)$$

$$I_2 = \sum_{\substack{i,j=1 \\ i \neq j}}^N \left\langle \psi_0 \left| \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_i^3 r_j^3} \right| \psi_0 \right\rangle, \quad (30)$$

and

$$I_3 = \int_0^\infty \ln r \frac{d^2 \rho}{dr^2} dr. \quad (31)$$

The term I_1 can easily be determined from the high-accuracy values of $\rho(0)$ for He and H^- calculated by Pekeris.^{12,15} Accurate values of I_2 and I_3 are not available in the literature for He and H^- and have been calculated in

the present work. Table IV lists the ground-state energy, I_2 , and I_3 as a function of basis size for He. Table V lists the same results for H^- . I_2 and I_3 have apparently converged to six digits for atomic helium and to almost four digits for the negative hydrogen ion. The accuracy achieved appears to be adequate for the present needs.

Using the "best-estimate" results of the expectation values listed in Tables IV and V, $S_f(3)$ may readily be calculated for He and H^- once the value of $N\rho(0)$ has been supplied. From the work of Pekeris the value of $N\rho(0)$ is known to be 45.501 for atomic helium¹² and 4.136 for the negative hydrogen ion.¹⁵ Hence the value of $S_f(3)$ is found to be 606.76 for He and 3.066 for H^- .

VII. THE CALCULATION OF THE EFFECTIVE DISTRIBUTIONS FOR He AND H^-

Effective distributions have been constructed according to the prescription given in Sec. III. The coefficients α and β of the first two terms in the asymptotic expansion and the moments of the oscillator-strength distribution which can be obtained from sum rules are listed in Table VI for He and H^- . The values of $S_f(3)$ listed are those which have been calculated in the present work. The values of $S(2)$, $S(1)$, and $S(-1)$ are expressible as expectation values of the wave function and have been taken from the work of Pekeris on atomic helium¹² and the negative hydrogen ion.¹⁵ $S(0)$ is, of course, equal to the number of electrons in the system, which is two for He and H^- .

Ab initio values of $S(-2)$, $S(-3)$, $S(-4)$, $S(-5)$, and $S(-6)$ have also been taken from the literature; however, these quantities cannot be expressed as expectation values of the wave function. These moments must be calculated variationally, hence the precision attained for $S(-2) - S(-6)$ is not likely to be as accurate as that of the $S_f(3)$, $S(2)$, $S(1)$, and $S(-1)$ calculations. The

TABLE X. Comparison of values of $L(k)$ for the negative hydrogen ion.

$L(-1)$	Source
-13.3	One-electron model ^a
-12.70	Consistent distribution ^a
-12.72	Present work ($M=4$)
-12.70±0.03	Present work (extrapolated)
$L(0)$	Source
-1.742	Consistent distribution ^a
-1.711	Present work ($M=4$)
-1.718±0.008	Present work (extrapolated)
$L(1)$	Source
0.6045	Consistent distribution ^a
0.4575	Present work ($M=4$)
0.4725±0.0075	Present work (extrapolated)
$L(2)$	Source
14.69	Consistent distribution ^a
16.62	Present work ($M=4$)
16.58±0.04	Present work (extrapolated)

^aReference 29.

values for $S(-2)-S(-6)$ have been obtained from the work of Langhoff *et al.*¹⁶ and Thakkar.¹⁷ Langhoff *et al.* performed calculations using two different basis sets for both He and H^- and generated "spectrum-a" and "spectrum-b" variational approximations to $S(-2)-S(-6)$. Thakkar has performed a calculation to obtain variational approximations to $S(-2)-S(-6)$ for He. Calculations of the effective distributions have been performed here using all of the above five sets of values. For atomic helium, Langhoff's spectrum-a values and Thakkar's values lead to effective distributions which are quite similar in appearance for the $M=1, 2, 3,$ and 4 cases. The effective distributions using the Langhoff spectrum-b values for the $M=3$ and 4 cases are considerably different from the corresponding effective distributions constructed from Thakkar's values and the spectrum-a values. In fact, for the spectrum-b effective distribution, the value of γ undergoes an unreasonably large jump between the $M=3$ and 4 cases. For this reason the results from the spectrum-b values for He have been disregarded. Moreover, the Thakkar values lead to a slightly better value of $L(2)$ (known from the accurate calculation of Schwartz¹¹) for the $M=4$ case than do the spectrum-a values. For this reason, for He, only the results obtained using the Thakkar values are presented here. For H^- , the effective distributions constructed from the spectrum-a and spectrum-b values for $S(-2)-S(-6)$ are extremely similar in appearance and the results obtained using the spectrum-a values have been rather arbitrarily chosen for presentation here. Table VII contains values of $S(-2)-S(-6)$ used for the construction of the effective distributions for both He and H^- . Table VIII contains the effective distributions for $M=4$ for both He and H^- .

In order to obtain the logarithmic mean excitation energies for atomic helium and the negative hydrogen ion it is necessary to insert the effective distribution into Eq. (18), as was done before atomic hydrogen. Tables IX and X contain the present results for He and H^- , respectively, along with various previous results. For each $L(k)$ is listed both the result from the $M=4$ distribution and an "extrapolated" value. The extrapolated value is an estimate obtained by examining the convergence of $L(k)$ for the $M=1, 2, 3,$ and 4 effective distributions and using the convergence behavior exhibited by the $L(k)$ for atomic hydrogen in Table I as a guide. Hence, the "extrapolated" value is somewhat subjective, but it is felt that such an estimate is useful and accurate to the error margin claimed in the tables.

Finally, the values of γ obtained from the calculations allow the high-energy oscillator-strength density to be written as a three-term asymptotic expansion. Of the three terms, the first two terms are correct, while the third term is somewhat of a "compromise"; i.e., to some extent the coefficient of the third term is such that the third term is attempting to reproduce all the remaining terms over the region where the effective density is nonzero. For He the recommended expansion is

$$\begin{aligned} \frac{df}{d\epsilon} = & 54.62(\epsilon - \epsilon_0)^{-7/2} - 242.7(\epsilon - \epsilon_0)^{-4} \\ & + 640.9(\epsilon - \epsilon_0)^{-9/2}, \end{aligned} \quad (32)$$

where $\epsilon_0 = -2.904$. For H^- the recommended expansion is

$$\begin{aligned} \frac{df}{d\epsilon} = & 1.241(\epsilon - \epsilon_0)^{-7/2} - 2.757(\epsilon - \epsilon_0)^{-4} \\ & + 3.346(\epsilon - \epsilon_0)^{-9/2}, \end{aligned} \quad (33)$$

where $\epsilon_0 = -0.5278$, with all quantities in Eqs. (32) and (33) in atomic units.

VIII. DISCUSSION

The calculations indicate that the effective oscillator-strength distributions suggested here provide an efficient means of evaluating various second-order properties for the systems considered here, and may possibly be useful for more complicated atoms and molecules. Although this technique does not allow the determination of bounds on the properties, as do certain other methods, this approach utilizes additional information about the high-energy behavior of the oscillator-strength distribution. For the evaluation of second-order properties which weight the high-energy oscillator strength heavily, such as $L(2)$, this additional information is important. It also appears that the effective distribution is capable of yielding a useful three-term expansion of the high-energy photoionization cross section in the dipole approximation, with the first two terms exact and the third term approximate. The interpretation taken here of the instability of the effective distribution obtained using the spectrum-b values for He is that these values were not adequately accurate enough to apply the proposed technique to such a high order, but this interpretation is open to question. It appears that caution must be exercised when constructing a distribution from many moments when the moments are not exact; more moments do not necessarily imply greater accuracy.

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