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The photodetachment cross section of the negative hydrogen ion*

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The photoionization cross section of the hydrogen negative ion is computed using a discrete-basis-set expansion to represent both the ground and continuum states of the system. This discrete-basis-set representation is used to construct an approximation to the dynamic polarizability, which in turn is used in an analytical continuation procedure for complex values of the frequency. This "discretization" of the continuum makes the method potentially applicable to larger systems, and a study of the basis-set dependence is made. The final results are in good agreement with more elaborate calculations and with experimental results. The dynamic polarizability in the normal dispersion region is also computed.

I. INTRODUCTION

The photoionization cross section of the hydrogen negative ion has been the subject of several calculations since Wildt[1] first suggested that it could be responsible for the visible and infrared opacity in the atmosphere of cooler late spectral type stars.

Chandrasekhar[2] and his co-workers pioneered these studies in a series of papers investigating the dependence of the cross section on the accuracy of the bound-state wave function. They also investigated the effect of the central field approximation for the free state.[3] The importance of taking into account exchange effects in the free wave function was first investigated by John[4] using the Hart-Herzberg 20-parameter wave function for the ground state and the "1*s*" exchange approximation continuum function. A number of subsequent calculations have appeared. Geltman[5] employed the 70-parameter bound-state wave function of Schwartz and variationally determined symmetrized continuum functions, containing terms corresponding to excited states of the hydrogen atom. This allowed him to treat both correlation and distortion of the residual hydrogen atom. Doughty *et al.*[6] employed a close-coupling approach for using a Hartree-Fock eigenfunction expansion for the continuum states which included up to 3*d* atomic orbitals of the hydrogen atom. Bell and Kingston[7] used the method of polarized orbitals to obtain a representation of the continuum. More recently Ajmera and Chung[8] used the variational method of Kohn-Feshbach to obtain free-state wave functions. A recent review of the photodetachment of H^- was given by Risley.[9]

While many of the above calculations have produced good results for H^-, they are generally not easily extended to large systems, first because such highly accurate wave functions are not available for systems with more electrons, and secondly because the generation of continuum functions by the methods used above becomes very cumbersome.[10]

Our interest is in developing a method which could be equally applied to larger systems. Thus we use highly accurate wave functions and methods practicable for polyatomic molecules, and we avoid the explicit use of continuum functions.[11] The method is based upon the relation between the cross section for photodetachment and the imaginary part of the frequency-dependent polarizability. As first suggested by Reinhardt and co-workers,[12(d)] we used a discrete basis-set representation of the frequency-dependent polarizability which is used to make an analytical continuation in the complex plane. Details of the method and the calculations are presented in Secs. II and III. This method has been successfully applied to other small systems,[12] but systematic studies of the basis set for the unbounded orbitals have not been reported. This is an important part of the problem since basis-set expansions represent the most convenient approach to the treatment of large systems. Once we understand how to select small but adequate basis sets for the unbounded orbitals, the method is automatically extendable to larger systems, since the use of basis-set expansions for the bound part of the system is well established.

II. METHOD

The basic difficulty with using a discrete or finite basis set for photoionization calculations is that we obtain only a finite number of transitions which are supposed to represent the continuum. That the discrete set does represent the continuum in some sense is indicated by the fact that the calculated sum over the discrete transitions (1) and its moments,

$$\sum_n f_{on} \tag{1}$$

(where f_{on} is the oscillator strength), is approximately equal to the integrated absorption for the continuum, (2), and its respective moments,

$$\int_{\epsilon_I}^{\infty} g(\epsilon)d\epsilon \tag{2}$$

[where ϵ_I is the ionization potential and $g(\epsilon)$ is the oscillator strength for the continuum]. On the other hand, it is clear that the oscillator strengths at every transition energy ω_{on} must be associated with a band of transition near ω_{on}. The problem then is how to proceed from the theoretical results

$$\{f_{on}, \omega_{on}, n=1, n_{\max}\} \tag{3}$$

to a continuum function $g(\epsilon)$.

The approach we follow makes use of the relationship between $g(\omega)$ and the complex dynamic polarizability $\alpha(z)$.

The frequency-dependent polarizability is given by

$$\alpha(\omega)=\sum_{n\neq 0}\frac{f_{on}}{\omega_{on}^2-\omega^2}+\int_{\epsilon_I}^{\infty}\frac{g(\epsilon)d\epsilon}{\epsilon^2-\omega^2}, \tag{4}$$

where f_{on} and $g(\epsilon)$ are the oscillator strengths for the bound and continuum transitions, respectively, ω_{on} the transition frequencies, and ϵ_I the first ionization threshold. Extending this definition to complex frequencies leads to

$$\alpha(z)=\sum_{n\neq 0}\frac{f_{on}}{\omega_{on}^2-z^2}+\int_{\epsilon_I}^{\infty}\frac{g(\epsilon)d\epsilon}{\epsilon^2-z^2}. \tag{5}$$

The complex polarizability $\alpha(z)$ is analytical throughout the complex plane except for an infinite number of poles along the real axis (the ones in the positive region corresponding to the transition frequencies) and a branch cut in the photoionization interval $\epsilon_I \leq \mathrm{Re}(z) < \infty$. Since the cross section can be written as[13]

$$\sigma(\omega)=(2\pi^2/c)g(\omega) \tag{6}$$

and since

$$\alpha(\omega+i\eta)=\sum_{n\neq 0}\frac{f_{on}}{\omega_{on}^2-\omega^2}+\mathrm{P}\int_{\epsilon_I}^{\infty}\frac{g(\epsilon)d\epsilon}{\epsilon^2-\omega^2}+i\frac{\pi g(\omega)}{2\omega}, \quad \text{as } \eta\to 0 \tag{7}$$

we obtain the relationship

$$\sigma(\omega)=\lim_{\eta\to 0}(4\pi\omega/c)\,\mathrm{Im}[\alpha(\omega+i\eta)], \tag{8}$$

between the total cross section and the imaginary part of the dynamic polarizability on the real axis.

So far we converted the problem of obtaining $g(\omega)$ to that of obtaining the imaginary part of $\alpha(z)$. This latter task is accomplished by an analytical continuation procedure[14] as follows: (i) we construct an initial guess for $\alpha(z)$ from Eq. (3) as

$$\alpha(z)=\sum_{n\neq 0}\frac{\tilde{f}_{on}}{\tilde{\omega}_{on}^2-z^2}; \tag{9}$$

this is approximate since each discrete $\tilde{f}_{on}$ represents a band of the continuum and thus should not be associated with a single $\tilde{\omega}_{on}$; (ii) using Eq. (9) we calculate $\alpha(z)$ at a number of points in the complex plane; (iii) these points are fitted by a Padé approximant, providing a representation of $\alpha(z)$ in the complex plane; (iv) using this representation we calculate $\alpha(z)$ on the real axis where it is equal to $\alpha(\omega)$; and (v) the imaginary part of $\alpha(z)$ on the real axis thereby provides the cross section by Eq. (8). Having the representation for $\alpha(z)$, we can evaluate $\sigma(\omega)$ at a very large number of points with little effort.

The crucial point in this process is the fitting procedure. In this respect it is important to notice that the analytical form of the frequency-dependent polarizability is such that it can be written as a Stieltjes series.[15] Consequently, Padé approximants[16] can be used as a very efficient way to perform the continuation. For this type of series, any sequence of $[N+J/N]$ Padé approximants (with $J \geq -1$) will converge, as N goes to infinity, to the function $\alpha(z)$ in the cut. Of course, we hope to achieve convergence with small values of N.

There are two ways of using Padé approximants to fit $\alpha(z)$. One is to use its analytical form and expand it in a Taylor series around some point z_0. The coefficients of the series can be used to construct the approximants by equating

$$f(z)=f(z_0)+a_1(z-z_0)+a_2(z-z_0)^2+\cdots+a_n(z-z_0)^n$$
$$=P_m/Q_n, \tag{10}$$

where P_m and Q_n are polynomials of degree m and n in $(z-z_0)$. Notice that for the particular case of $f(z)=\alpha(z)$ and z_0 chosen at the origin, the coefficients a_i are the sum rules. Although the approximants are determined by the information in $f(z)$ at only one point, these unipoint-multipiece approximants have been successfully used to continue Taylor-series expansions out of its range of convergence. In addition, inside the circle of convergence of the Taylor series, they usually converge faster than the series itself. Among several applications, this type of Padé approximant has been used to calculate second-order optical properties of atoms and molecules.[17] However, there are some cases where this type of Padé approximant presents numerical problems. For example, small errors in the coefficients can produce uncontrollable divergences far from the point of expansion. This implies that the use of higher-order Padé approximants (to obtain better convergence) can be seriously affected by increasing error in the coefficients.[18]

This type of divergence can be circumvented by the use of multipoint-multipiece Padé approximants. In these cases, instead of expanding the function around one single point, we expand it at several points, with a subsequent matching of the series. The extra points can be picked, for instance, in the regions where the Padé approximant constructed from the previous series starts diverging. Multipoint-multipiece Padé approximants have been the subject of recent theoretical investigations,[19] mainly in their relation to Stieltjes series, and many of the results for the normal Padé approximant can be extended to the multipoint case. Several recent applications of two-point Padé approximants have been reported in the literature.[20] In principle, this type of Padé approximant should provide the best way of fitting the function since it contains several pieces of information about the function at each point. Increasing the number of points leads to additional algebra involved in the matching of the various series. Here, the approach is most useful if a small number of points is sufficient to assure convergence over the range of interest.

An alternative approach is to construct a Padé type-II approximant.[21] This Padé approximant is built not from the coefficients of a Taylor-series expansion but from values of the function at different points. In the nomenclature used above, this is a multipoint-unipiece Padé approximant, and is the type of Padé approximant used in the present work. Here we do not have problems associated with uncertainties in the coefficients. Besides that, since we can, in principle, pick points covering most of our range of interest, it seems to be more efficient for the continuation than the usual unipoint-multipiece Padé approximant.

III. WAVE FUNCTIONS AND BASIS SETS

A. Wave functions

The Hartree-Fock wave function of H^- is unbounded, i.e., above the energy of the H atom, and hence inappropriate to our studies. The simplest acceptable wave function is the five-term expansion:

$$\psi(^1S) = c_1\phi_{1\bar{s}}^2 + c_2\phi_{2\bar{s}}^2 + c_3(\phi_{2\bar{p}x}^2 + \phi_{2\bar{p}y}^2 + \phi_{2\bar{p}z}^2). \qquad (11)$$

We solved for the orbitals and coefficients of this MC-SCF wave function using the GVBTWO program.[22] The resulting energy is −0.5251 hartree which is 0.0026 hartree (0.07 eV) above the exact energy but 0.0372 hartree (1.012 eV) below the Hartree-Fock energy.

As an approximation to the ^1P continuum states, we solved for the wave functions

$$\psi(^1P) = \phi_{1s}\phi_{npz} + \phi_{npz}\phi_{1s}, \qquad (12)$$

where ϕ_{1s} is taken as the 1s orbital of the hydrogen atom and ϕ_{npz} are the variational solutions of Eq. (12) (given fixed ϕ_{1s}).

The final wave functions for the calculation were obtained from CI calculations using the above orbitals.[23] For the ^1S state we used the five orbitals from Eq. (11) plus the ϕ_{1s} orbital from Eq. (12) (orthogonalized), including all the allowed configurations (nine configurations). For the ^1P states we included the nine p_z orbitals from Eqs. (11) and (12) plus the three s orbitals ($\phi_{1\bar{s}}, \phi_{2\bar{s}}, \phi_{1s}$), allowing a full CI over these states (27 configurations).[33] These solutions were used to evaluate the oscillator strengths for the various $^1P \leftarrow {}^1S$ transitions. The basis set is discussed below.

B. Basis sets

All calculations were carried out using the Huzinaga [6s/3s] expansion for the 1s orbital ($\zeta = 1.0$) plus the inner two components of the (4p) expansion of the 2p orbital ($\zeta = 0.5$).[24] To this basis set we added diffuse s and p basis functions, as indicated below.

The uncertainty in choosing the basis set concerns what to include for the continuum wave functions. We cannot optimize the basis sets as we do for bound states. Instead we want an expansion leading to a good description of (at least) the region of the continuum most involved in the process. One criterion which we used to determine the quality of the basis sets is to require them to produce a distribution of oscillator strengths and transition frequencies which satisfy the sum rules (see Sec. IV B for a discussion of the sum-rule criterion).

It is important in this type of study to have a systematic way of changing both the number of basis functions and the range of exponents of the basis sets. We accomplished this by considering each member of the diffuse s and p basis sets to have orbital exponents as

$$\zeta, \beta\zeta, \beta^2\zeta, \ldots,$$

that is, each orbital exponent is the geometrical factor β times the previous exponent. Various geometrical factors, β, were used with diffuse s and p functions lying in the range 0.04–0.002 56. Explanatory calculations indicated that the diffuse s and p basis functions should have the same distribution of exponents, and hence we took

$$\beta_s = \beta_p.$$

In Table I we show the spectra (f_{on} and ω_{on}) resulting from three different basis sets, all covering the same range (out to 0.002 56) in exponents. From this table it is clear that the smoothest spectrum is the one generated by the basis set [11s/

TABLE I. Dependence of the spectra upon basis set.[a] f_{on} is the oscillator strength, ω_{on} the transition energy (eV).

$[7s/7p;\beta=1/2.5]$		$[9s/9p;\beta=1/1.75]$		$[11s/11p;\beta=1/1.5]$	
f_{on}	ω_{on}	f_{on}	ω_{on}	f_{on}	ω_{on}
0.043039	0.841215	0.025572	0.813537	0.017101	0.793612
0.215733	1.250041	0.114370	1.082266	0.076601	1.002800
0.454171	2.279275	0.246037	1.585558	0.168768	1.356880
0.437477	4.896766	0.294583	2.495641	0.212764	1.916556
0.418858	11.379151	0.322565	4.155460	0.250749	2.784818
0.051405	63.118341	0.282310	7.315295	0.228296	4.140133
		0.108864	14.017534	0.227801	6.289182
				0.211064	9.859149
				0.137689	16.633445

[a] The diffuse functions of these three basis sets cover the exponent range of 0.04–0.00256 for both s and p spaces. Since the geometrical factors are different, the first diffuse basis of each basis set are not exactly equal. They are 0.04000, 0.04202, and 0.04374 for $\beta=1/2.5$, 1/1.75, 1/1.5 respectively.

$11p$; $\beta=1/1.5$]. Of course smoothness is not a rigorous criterion for choosing a basis. A more fundamental criterion is the agreement with the sum rules arising from the spectra. We proceeded then by computing the sum rules for several basis sets using various sized basis sets with various geometrical factors. In some cases the s basis set was insufficient to describe the ground-state ^1S, and the basis set was discarded.

Table II shows some typical results for several cases. For the three basis sets of Table I (which cover essentially the same range of exponents), we see that $[7s/7p;\ \beta=1/2.5]$ exceeds sum rules S_1, S_2, and S_3, while both $[9s/9p;\ \beta=1/1.75]$ and $[11s/11p;\ \beta=1/1.5]$ exceed the S_2 and S_3 sum rules. On the basis of this comparison, $[7s/7p;\ \beta=1/2.5]$ is clearly unsatisfactory.

TABLE II. Sum-rules dependence on the basis sets.

Basis sets	S_0	S_1	S_2	S_3
$[7s/7p;\beta=1/2.5]$	1.625	15.06	228.1	4535.4
$[7s/9p;\beta=1/2.5]$	1.574	14.95	227.9	4537.6
$[9s/9p;\beta=1/2.5]$	1.574	14.96	227.9	4526.3
$[7s/7p;\beta=1/1.75]$	2.048	15.61	228.9	4536.8
$[9s/9p;\beta=1/1.75]$	1.394	14.54	226.5	4505.4
$[11s/11p;\beta=1/1.75]$	1.849	15.44	228.3	4505.1
$[11s/11p;\beta=1/1.5]$	1.531	14.81	227.2	4511.4
$[9s/11p;\beta=1/1.5]$	1.829	14.84	210.7	3983.7
$[7s/11p;\beta=1/1.5]$	1.51	14.2	208.3	3940
Bounds	2	15.0[a]	217 ± 7[b] 206.0[c]	4000 ± 300[b]

[a] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

[b] C. Schwartz (unpublished) (cited in Ref. 5).

[c] Reference 28.

We next considered variations in the number of s and p basis sets while keeping β fixed. From Table II it is clear that (a) for the geometrical factor $\beta=1/2.5$ no improvement is obtained; (b) for $\beta=1/1.75$, the addition and subtraction of basis functions to the basic $[9s/9p]$ basis do not show any improvement; on the contrary, worse sum rules are obtained; (c) for $\beta=1/1.5$ substantial improvement is obtained when the number of basis sets of the s space is reduced.

On these considerations we selected $\beta=1/1.5$ as the optimum geometrical factor. Figure 1 shows the resulting cross sections for some of the bases which violated the sum-rule criterion.

Once the optimum geometrical factor was chosen, we turned our attention to the size, i.e., the number of basis functions in the basis set. Assuming

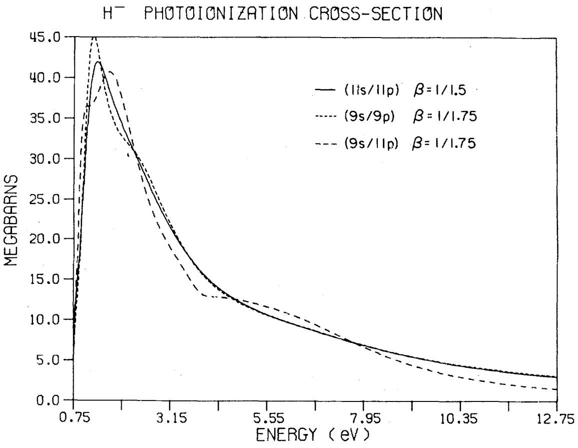

FIG. 1. Effect of different basis sets on the photoionization cross section of H^-.

TABLE III. Energy of the ground state ^1S of H^- for various basis sets ($\beta = 1/1.5$).

Basis sets	Energy (hartree)
$(11s/11p)$	−0.525099
$(9s/11p)$	−0.525098
$(7s/11p)$	−0.525097
$(6s/11p)$	−0.524980
$(7s/11p)$ after CI	−0.525494
Hartree Fock[a]	−0.487930
Weiss $S+P$[b]	−0.526470
Exact[c]	−0.527750

[a] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

[b] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[c] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

that we have enough diffuse p functions in the basis set, the question to be answered is how many s diffuse functions are required? Table III shows the dependence of the H^- ground-state energy on the size of the s basis, for $\beta = 1/1.5$, using the basis sets listed in Table IV. From Table III we see that only $7s$ basis functions are required. We selected this basis set $[7s/11p, \beta = 1/1.5]$ as the optimum one. This basis set was the one used for the calculations of the cross sections and dynamic polarizability.

IV. RESULTS

The final spectra obtained are shown in Table V. These spectra were used to produce all the results described below.

TABLE IV. Largest basis set used $(11s/11p)$ with the best geometrical factor $\beta = 1/1.5$. Exponents above the solid line are contracted together with relative coefficients as in the H-atom basis functions. Exponents below the dotted lines are considered as diffuse functions (modified in various basis sets).

s exponents	p exponents
68.16	0.73
10.2465	0.17
2.34648	0.113
0.67332	0.04374
0.22466	0.02916
0.082217	0.01944
0.04374	0.01296
0.02916	0.00864
0.01944	0.00576
0.01296	0.00384
0.00864	0.00256
0.00576	
0.00384	
0.00256	

TABLE V. Spectrum obtained with the $(7s/11p)$ basis set. Oscillator strengths $\tilde{f}_{on}$ and transition frequencies $\tilde{\omega}_{on}$.

$(\tilde{f}_{on})_{\text{length}}$	$(\tilde{f}_{on})_{\text{velocity}}$	$\tilde{\omega}_{on}$ (eV)
0.00888214	0.00869698	0.79335322
0.06835403	0.06603274	1.00254140
0.15545195	0.15523099	1.35662122
0.22477895	0.22949153	1.91629754
0.24558997	0.24070119	2.78455907
0.23131597	0.23283304	4.13987423
0.22792494	0.22992260	6.28895075
0.20792662	0.20578687	9.85880897
0.13857175	0.13693591	16.63336036

A. Cross section for photodetachment

Following the procedure outlined in Sec. II, we performed the analytical continuation to obtain the cross sections. Figure 2 shows the results for two different analytical continuations, indicating the convergence of the calculation. The convergence is good for both velocity and length forms. Figure 3 shows our results in both forms compared with other theoretical results. The agreement among all calculations is good in general except in the region very near the threshold. Our best agreement over the entire range (Fig. 3), in both forms, is with Geltman,[5] who used true continuum wave functions in his calculations. This suggests that we are representing the continuum well, at least for the region most involved in the process.

Comparing our results with the experiment in

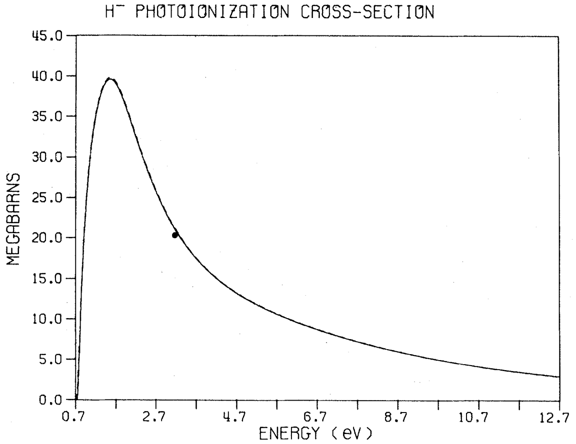

FIG. 2. Dependence of the calculated H^- photoionization cross section on different analytical continuations (dipole velocity form). The points in the complex plane used to calculate $\alpha(z)$ were chosen as previously [Refs. 12(a)–(c)] with $\text{Re}(z_i) = (\omega_{0i+1} - \omega_{0i})/2$ and $\text{Im}(z_i) = R(\omega_{0i+1} - \omega_{0i})$. The figure shows results for $R = 0.75$ (solid) and $R = 1.00$ (dashed). No appreciable changes are noticed as long as the points are near the real axis.

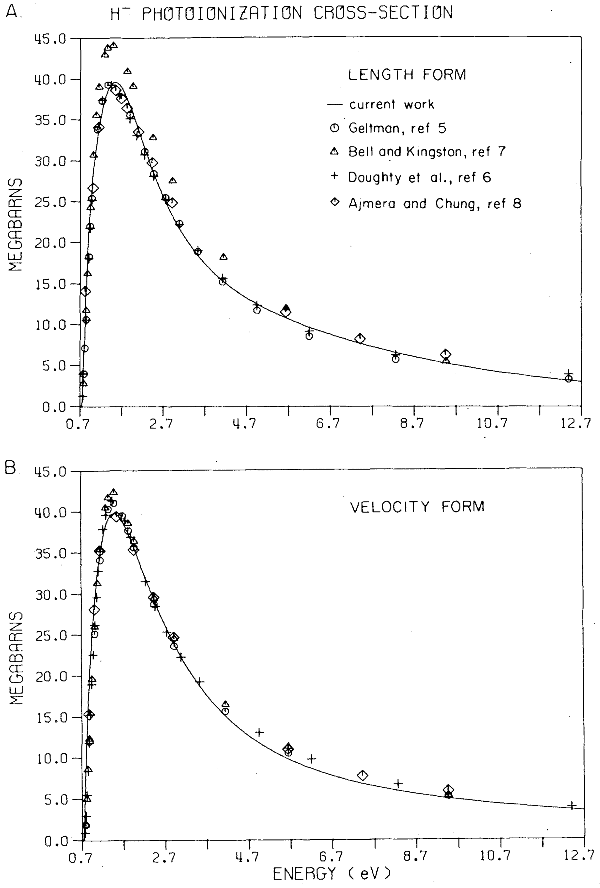

FIG. 3. Comparison among calculated photoionization cross sections for H⁻ using both (*A*) the length and (*B*) velocity forms for the transition matrix elements.

Fig. 4, we find good agreement. These experimental results are the relative measurements of Smith and Burch[25] normalized to the value of our cross section at 2.35 eV (5280 Å). These relative measurements have a maximum estimated uncertainty of ±3%. On the basis of the absolute integrated measurements of Branscomb and Smith,[26] Geltman put Smith and Burch's results on an absolute basis, obtaining a value of 32.8 Mb at 2.35 eV (5280 Å), with an uncertainty of 20%. This value is in good agreement with our value of 30.56 Mb at 2.35 eV (5280 Å).

From Fig. 4 we also see that the agreement between the length and velocity forms of the cross sections is very good. Since for the exact wave functions $\Psi(^1S)$ and $\Psi(^1P)$ these two forms are equivalent, the agreement between them can be used as a test for the quality of the basis set. Of course close agreement between the two forms is only a necessary but not sufficient condition for an adequate basis set.

B. Sum-rules

One way of estimating the quality of our results is to compute the sum rules associated with each distribution. Because the sum rules emphasize different regions of the spectra, they provide an estimate of the accuracy of the cross section at different values of energy. On the basis of the sum-rules criterion, Dalgarno and Kingston[27] were able to show that the cross sections calculated by Chandrasekhar should be in error. Geltman[5] analyzed his results in terms of his sum rules and concluded that his results should be low near the threshold. These sum rules can be expressed as

$$S_k=\sum_{n\neq 0}\frac{f_{on}}{\omega_{on}^k}. \tag{13}$$

S_0 is the Thomas-Reich-Kuhn oscillator-strength sum rule and S_2 is the static polarizability. The exact values of these sum rules contain contributions not only from transitions in which the hydrogen atom is left in its ground state, but also from transitions in which the hydrogen atom is left in an excited state or even ionized. Thus the exact values can be used as upper bounds for the values computed when only the transitions leaving the hydrogen atom in its ground state are considered. Table VI shows our sum rules compared with other calculations and with the upper bounds. Note that most results in Table VI are for the single-channel in which the H atom is left in the 1*s* state, whereas the bound includes all processes. Thus theoretical values of S_i close to the bound need not indicate an accurate result.

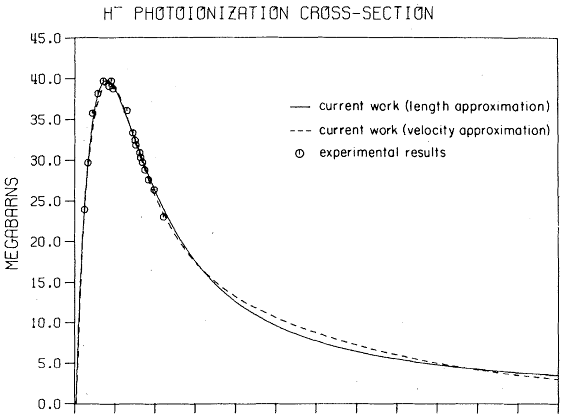

FIG. 4. Comparison of theoretical and experimental photoionization cross sections for H⁻. Experimental points are relative measurements of Smith and Burch, Ref. 25, normalized to the value of our cross section at 2.35 eV (5280 Å). Solid line, dipole length form; dashed line, dipole velocity form.

TABLE VI. Sum rules for H⁻ [see Eq. (13)]. Except as noted,[h] all theoretical results are for the single channel in which the H atom is left in the 1*s* state. Thus the S_i should be less than the bound (which includes all processes).

	S_0		S_1		S_2		S_3	
	Length	Velocity	Length	Velocity	Length	Velocity	Length	Velocity
Geltman[a]		1.72	14.0[f]	14.2	198[g]	202.4	3570[g]	3742
Doughty *et al.*[b]			14.4	14.2	201	202	3630	3720
Bell and Kingston[c]			14.7	16.0	205	227	3700	4150
Langhoff *et al.*[h]	1.99		14.95		206.1			
Present work	1.51	1.50	14.2	14.1	208.3	206.8	3940	3894
Bounds	2		15.0[f]		217 ± 7[d] 206.0[e]		4000 ± 300[d]	

[a] Reference 5.

[b] Reference 6.

[c] Reference 7.

[d] C. Schwartz (unpublished) (cited in Ref. 5).

[e] Reference 28.

[f] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

[g] From Ref. 7.

[h] Reference 11(d). These sum rules include the process where the residual hydrogen atom is left in the 2*s* excited state.

Assuming Schwartz's bound for the static polarizability, Table VI shows that all the sum rules are satisfied. On the other hand, if Chung's[28] value is taken for the upper bound, we exceeded this value in both forms. This may indicate that the cross sections near threshold are somewhat large. Independently of which bound is used for the static polarizability, other calculations seem to indicate low values of the cross section near threshold. Consequently we expect the exact values near the threshold to lie somewhere between our results and the other calculations.

C. Dynamic polarizability

An alternative way of checking our distribution is to calculate the dynamic polarizability in the normal dispersion region below the threshold. Since there are no bound-bound transitions for H⁻, it can be seen from Eq. (7) that both the real and imaginary parts of the dynamic polarizability are given directly by $g(\omega)$.

In general, there are several alternate approaches to extracting the information contained in the frequency-dependent polarizability. First of all, if there is interest only in the absorptive properties of the system, we can neglect all the bound-bound transitions because the imaginary part of $\alpha(z)$ is given solely by the distribution $g(\omega)$ which only involves bound-free transitions. Indeed, in the case of the hydrogen atom,[12(d)] a better description of the cross section was obtained when two bound-bound transitions were neglected. Another possibility is to construct the full representation for $\alpha(z)$ including all bound-bound transitions. In this case we can extract from $\alpha(z)$ both the dispersive and absorptive properties of the system. There is still another possibility which is to use the real part of $\alpha(z)$. Since it is directly related to the index of refraction by

$$n(\omega) - 1 = 2\pi N_0 \operatorname{Re}[\alpha(\omega)], \qquad (14)$$

we could, in principle, use experimental index-of-refraction data and discrete oscillator strengths to perform the analytical continuation. Unfortunately these data are not accurate enough to produce good cross sections.[12(d),29]

Figure 5 shows our results for the dynamic polarizability compared with a variational-perturbation calculation by Chung.[28] The curves parallel Chung's values up to 0.01 h and begin to deviate significantly above 0.023 hartree. Near the threshold (0.0275 hartree) the difference is very large. Although Chung's results are expected to be very accurate for lower energies (where they are converged values for a 140 Hylleraas-type wave function), they are not converged for $E > 0.023$ hartree (just the region where our values start deviating significantly from Chung's). While it is clear from Chung's results that inclusion of more terms in the expansion would not affect this region drastically,

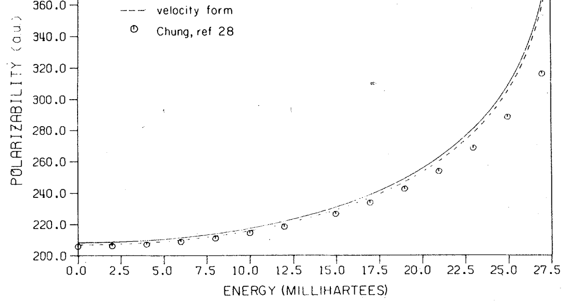

FIG. 5. Theoretical dynamic polarizabilities.

it is important to note that his wave function is contracted and cannot describe well the behavior of a diffuse system such as H^- near the threshold. (this is clear from Chung's results for Li^+, a much tighter system, where a rapid increase in the region near the threshold is found and a faster convergence is obtained.) More recently, Adelman[31] developed an analytical expression for the dynamic polarizability of H^-, using Rotenberg and Stein's[32] wave function (a 33 Hylleraas term expansion plus a tail function) and an asymptotic approximation. His value for the static polarizability was 215.5 a.u., but if he uses Chung's value of 206 a.u., his results differ from Chung's results by about 4.5–5.0% for $\omega \geqslant 0.025$ hartree. Very close to threshold this difference jumps to 6.6%, his value being larger than Chung's, but still much lower than our present results. We believe that this large discrepancy near threshold is due to the fact that Adelman's expression for $\alpha(\omega)$ is poleless, which could prevent it from increasing sufficiently in the region very close to threshold. Thus, while we expect Chung's value of the static polarizability to be more exact, we expect our dynamic polarizability to show a more correct behavior over the whole range.

Based on all the results presented above, we conclude that the velocity form of the frequency-dependent polarizability gives the best results, but that the agreement with the results from its length form is very good.

V. CONCLUSIONS

The results obtained permit us to conclude that a discrete-basis-set expansion can be effectively used to represent the continuum wave functions. This "discretization" of the continuum together with techniques of analytical continuation can be efficiently used to calculate cross sections for photoionization, once an adequate basis set is chosen. That makes the method potentially applicable to large systems.

For H^- there remains some uncertainty about the region near the threshold. This region remains unexplored experimentally. Although the uncertainty is not great enough to invalidate any conclusions about the importance of photoionization in H^-, it seems that the subject merits a new experimental investigation, using modern techniques such as tunable dye lasers and modern systems of detection.[30]

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