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Two-photon detachment of H^-

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A precision calculation of the two-photon detachment cross section for H^- is performed by means of a non-Hermitian Floquet theory. A highly accurate initial state wave function is used along with fully correlated saddle-point wave functions for the intermediate and final states. The cross section is investigated for energies below the $n=2$ and $n=3$ thresholds. The peak cross section predicted for the ^1D resonance is 3.10×10^{-49} cm^4 sec at 10.873 2 eV. It represents an *ab initio* theoretical prediction in complete agreement with the experimental result of 3.2 $(+1.8,-1.2)\times10^{-49}$ cm^4 sec at 10.873 2(27) eV.

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Since the advent of high-intensity lasers, multiphoton processes have been a subject of intense interest in the literature. In general, these processes are strongly affected by intermediate- as well as final-state resonances. The resulting spectra could be very complicated. In this regard, the H^- system is of particular interest to theorists due to the absence of excited bound states. Various (perturbative or nonperturbative) theoretical methods have been used to study the multiphoton detachment cross section of this system [1–7]. There has been also a number of two-photon detachment cross section (TPDCS), σ_2, experiments for H^-, both above and below the single-photon detachment threshold [8–11] mainly in the weaker field or perturbative regime. In particular, a prominent ^1D resonance structure above this threshold has been observed in the experiment [8] and predicted by theory [4–6]. The latest measurement [10] yields a peak σ_2 of $3.2(+1.8,-1.2)\times10^{-49}$ cm^4 sec or 420 $(+240, -160)$ (Γ/I^2) a.u., whereas the theoretical predictions are 703 [5] and 710 [4] (Γ/I^2) a.u. Γ is the width and I is the radiation intensity. Hence, despite the rather large error bars quoted in the experiment, the existing theoretical data still fall outside of the experimental uncertainty. In this work, we advance this field by performing a precision calculation of σ_2, combining the non-Hermitian Floquet formalism [12,13] with the complex-scaling saddle-point technique [14] using highly accurate wave functions for intermediate and final states. The calculated results provide a theoretical prediction that is in close agreement with the experiment [10], well within the quoted experimental uncertainty.

In this work, we extend the non-Hermitian Floquet matrix formalism to study the TPDCS of H^-. This method has been adopted for the study of multiphoton processes by many authors [12]. However, most of the applications did not explicitly include correlation. In Chu and Reinhardt [13], the non-Hermitian Floquet matrix method is developed and applied to the hydrogen atom in a strong field. In this case, a large number of Floquet blocks are needed in the computation. For weaker fields, the structure of the Floquet Hamiltonian can be greatly simplified. In the case of an *S*-wave ground state such as H^-, we can approximate the Floquet Hamiltonian by

$$|H_{ij}^F| = \begin{vmatrix} |H_0-E| & |V_{sp}| & 0 \\ |V_{sp}| & |H_0-E-\omega| & |V_{pl}| \\ 0 & |V_{pl}| & |H_0-E-2\omega| \end{vmatrix} = 0. \tag{1}$$

Here ω is the photon energy, l is either s for the *S*-wave final state or d for the *D*-wave final state, $|V|$ implies a matrix of V, and H_0 is the nonrelativistic Hamiltonian for H^-. The perturbation potential H' with a field strength F in the dipole approximation is

$$H' = 2\mathbf{F}\cdot\sum_i \mathbf{r_i}\cos(\omega t) = 2V\cos(\omega t). \tag{2}$$

In principle, the H_{11}^F block should be constructed with a set of *S*-wave basis functions. To fully account for the correlation of H^-, it needs a very large basis set that increases the size of the matrix of Eq. (1) substantially. However, for ground-state absorption in a weak field ($F=0.0001$ a.u. is used in this work), this basis set can be replaced by a highly accurate ground-state wave function. Hence, the H_{11}^F block is reduced to a 1×1 matrix. This greatly simplifies the calculation. In this work, we used a 386-term multiconfiguration interaction (MCI) wave function as in Kuan *et al.* [15]. The energy of this wave function is $-0.527\,737\,15$ a.u. This is slightly higher than the exact nonrelativistic ground-state energy. However, it happens to be the exact energy when relativistic and mass polarization corrections are included.

The H_{22}^F block is constructed with MCI basis functions of *P* symmetry. This wave function is used to represent the intermediate state. In this work, the σ_2 for energies both above (AT) and below (BT) the single photon detachment threshold are considered. Entirely different intermediate-state basis functions are used for the two energy regions. For BT, an 144-term MCI wave function is used. The nonlinear parameters in these basis functions are optimized to improve convergence. Since the photon energy for this region ranges from 0.014 to 0.0277 a.u., the nonlinear parameters were optimized by maximizing the dynamic polarizability of the

TABLE I. H^- ^1S and ^1D resonances below the H ($n=2,3$) thresholds (in μa.u.); E_{rel} is the relativistic corrections of p^4, Darwin term, *e-e* contact term, and orbit-orbit interaction. E_{mp} is the mass polarization correction. E_T is the energy above the H^- ground state at $-0.527\,737\,15$ a.u.

	$-E_{nonrel}$	E_{rel}	E_{mp}	$-E_{tot}$	E_T (eV)	Γ (meV)
			Below $n=2$ of H			
^1D	127 930.3	−1.02	−3.71	127 935.1	10.873 2	8.634
$^1S(1)$	148 800.2	−1.65	1.12	148 800.7	10.305 8	47.52
$^1S(2)$	126 020.0	−1.62	0.06	126 021.6	10.925 3	2.483
			Below $n=3$ of H			
$^1D(1)$	65 950.3	−0.35	−0.86	65 951.5	12.559 0	44.8
$^1D(2)$	56 810.3	−0.41	−0.20	56 810.9	12.807 6	6.69
$^1D(3)$	55 752.2	−0.41	−0.03	55 752.7	12.836 4	1.20
$^1D(4)$	55 698.1	−0.34	0.12	55 698.3	12.837 8	1.01
$^1S(1)$	69 001.1	−0.52	0.03	69 001.6	12.476 0	38.6
$^1S(2)$	57 773.2	−0.51	−0.15	57 773.9	12.781 4	8.27
$^1S(3)$	56 091.7	−0.30	2.58	56 089.4	12.827 2	2.65
$^1S(4)$	56 000.1	−0.51	0.07	56 000.5	12.829 6	1.09
$^1S(5)$	55 648.5	−0.52	−0.01	55 649.0	12.839 2	0.35

ground state at $\omega=0.021$ a.u. The same *P*-symmetry wave function is used for both the *D*- and *S*-wave final-state calculations.

For the H_{33}^F block, the wave function must properly represent the final state in the continuum. It can be separated into closed- and open-channel parts. The saddle-point wave function [16] is used for the closed channel, whereas the open channel is handled by complex scaling similar to that of Chung and Davis [14]. For the *D*-wave final state, we used 150 terms for the closed channel, and for the *S*-wave final state, we used 108 terms for the closed channel. 1*s* vacancies are built into these functions using the saddle-point method. The open channel is simply a hydrogen 1*s* state multiplied by a series of Slater orbitals as in Chung and Davis [14]. These wave functions yield highly accurate energies and widths for the ^1D and ^1S resonances. These results are given in Table I. We should mention that there is a great deal of theoretical and experimental data on the ^1D and ^1S H^- resonances in the literature; many of these references can be found in Rislove *et al.* [10]. Since the main interest in this work is TPDCS, they are not included in Table I for comparison.

The complex scaling technique is applied to Eq. (1). By solving for the ground-state eigenvalue $(E_r - i\Gamma/2)$ we can calculate the σ_2 in a.u. from Γ/I^2, which is independent of the radiation intensity *I* in the weak-field limit. To convert to cm^4 sec, this value is multiplied by ω^2. Calculations are done for both the *S*- and *D*-wave final states. The total rate is obtained by direct summation. Since Γ varies as F^4 for TPDCS, it is very small compared with E_r. To ensure numerical reliability, quadruple precision arithmetic is used in solving Eq. (1).

There are a number of theoretical BT TPDCS data in the literature [1,3,4,7] for H^-, but some discrepancy still exists among different calculations. We compare our result with some of those in Fig. 1. The agreement with Geltman [1] and Laughlin and Chu [7] is quite good, except that our data show a bump that is absent in these references. This bump is the result of summing the very different *S*- and *D*-wave cross section that intersects (see Fig. 1). The results of Shakeshaft and collaborators [4] also generally agree well with the present work and their data show a similar bump in the total TPDCS.

The result in Fig. 1 was calculated with an $F=0.0001$ a.u. However, if we double or halve this field strength, the resulting TPDCS remains the same, except when ω is very close to the threshold where σ_2 becomes intensity dependent. These results are also very stable with respect to the number of terms in the *P*-wave as well as in the final-state wave functions. For example, if we reduce the number of terms in the *P*-wave or in the final-state wave functions from what we used by about 1/4, the changes in σ_2 are generally much less than 5%.

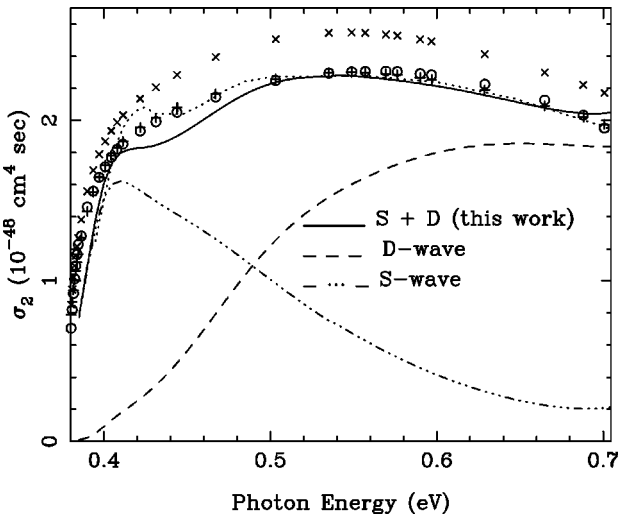

FIG. 1. TPDCS of H^- for photon energy below the single-photon detachment threshold. Circles, Ref. [1]; ++, Ref. [7]; crosses, Ref. [3]; dotted line, Ref. [4]; solid line, this work.

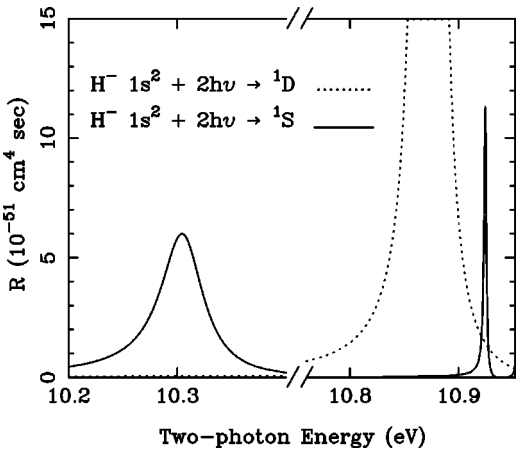

FIG. 2. TPDCS of H^- near the ^1S and ^1D resonances. The peak for the ^1D resonance is much higher than the scale in this figure.

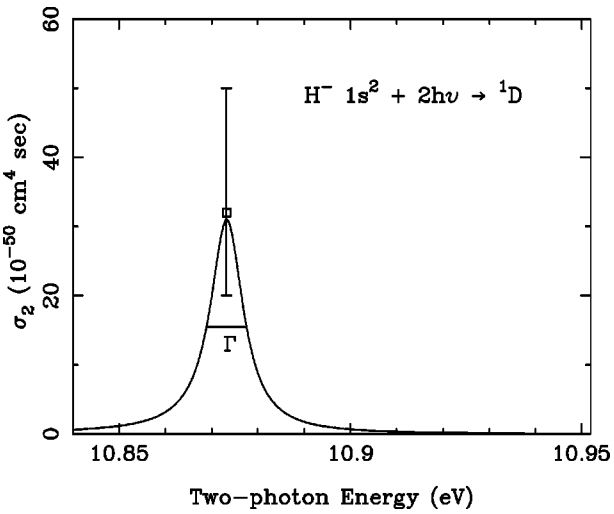

FIG. 3. TPDCS of H^- near the ^1D resonance, experimental data from Rislove *et al.* [10]. Γ is plotted at half maximum using the energy and width data from Table I. $\Gamma_{expt}=8.9(12)$ meV, $\Gamma_{theor}=8.634$ meV; $E_{res}^{expt}=10.8732(27)$ eV, $E_{res}^{theor}=10.8732$ eV.

For the TPDCS in the AT energy region, the intermediate states are in the continuum. We need a *P*-symmetry wave function to properly represent this continuum. This can be done by using the saddle-point wave function, as in the case of *D*- and *S*-wave final states. However, in principle, the Γ calculated with Eq. (1) includes both the single-photon detachment rate (SPDR) as well as two-photon detachment rate. In fact, as long as the SPDR is present, it will be the dominate contribution to Γ. Hence, in order to calculate σ_2, we must remove the SPDR contribution to Γ. This can be accomplished by removing the open channel and only keeping the closed-channel segment in the intermediate *P*-wave function. This eliminates the two-photon process of successive single-photon absorption, which is important near the single-photon detachment threshold. But, it should be an excellent approximation near the resonance region. In this work a 129-term saddle-point wave function is used. A similar wave function has recently been used for the single-photon detachment and resonances of H^-. Highly accurate results were obtained [15].

With the same final-state *D*- and *S*-wave functions used in the BT case, we carry out the TPDCS calculations. The results are shown in Fig. 2. These results are independent of the field intensity and very stable. The first ^1S resonance is rather broad, the TPDCS peak is 6.01×10^{-51} cm^4 sec occurring at about 5.1522-eV photon energy. The width of the second ^1S resonance is much narrower and the TPDCS peak is more than twice that of the first ^1S resonance. This second ^1S resonance was not observed in some of the previous calculations [3,4]. The TPDCSs of both ^1S resonances are smaller than that of the ^1D resonance by more than one order of magnitude. The physical reason behind these results can be understood from an independent-particle picture. It is easy to excite the $1s1s$ ^1S to $2p2p$ ^1D state with two photons. On the other hand, the $2s2s$ ^1S state can only be reached through correlation and configuration mixing. The corresponding oscillator strength is much smaller. The width of the first ^1S resonance is larger than that of ^1D by a factor of 5.5, implying that the smaller oscillator strength needs to cover a much larger energy region. This explains why the TPDCS peak is so low for the ^1S resonance.

The TPDCS, energy, and width measurements for the ^1D resonance have been made by Stintz *et al.* [8]. More recently, a new measurement was done by the same group [10]. In this latter experiment, the energy and width have been determined to be 10.873 2(27) and 0.0089(12) eV, respectively. The absolute TPDCS peak for this resonance is also determined to be 3.2 $(+1.8,-1.2)\times10^{-49}$ cm^4 sec. These results agree closely with the 10.873 2 eV, 8.634 meV, and 3.10×10^{-49} cm^4 sec predicted in this work. In Fig. 3 we show the calculated ^1D-resonance line profile with the TPDCS peak compared with experiment. To our knowledge, this is the first theoretical prediction of TPDCS of ^1D resonance that is well within the experimental error bar. We should point out that the resonance widths in Table I are calculated with the standard saddle-point complex-rotation method [14]. The apparent width in Fig. 3 agrees completely with Table I.

Among the many H^- ^1D theoretical work in the literature (see Ref. [10]), the energy and width predictions closest to our results are those of Chen [17] (10.873 2 eV, 8.651 meV) and Ho [18] (10.872 9 eV, 8.601 meV). The former uses *B*-spline functions and the latter uses correlated coordinate basis functions. Both are very large complex-rotation calculations.

It would be of interest to see whether there are other higher prominent resonances that may be good candidates for σ_2 measurements. To answer this question we compute the σ_2 below the $n=3$ threshold of hydrogen. For the *S*-wave final state, a 113-term MCI function is used for the closed channel; three open channels ($1sks$, $2sks$, $2pkp$) are included in the total wave function. For the *D*-wave final state, a 141-term wave function is used for the closed channel; four open channels ($1skd$, $2skd$, $2pkp$, $2pkf$) are included in this total wave function. The same 129-term *P*-wave intermediate state is used. In this energy region, we found five ^1S and four ^1D resonances. The energy and width results are included in Table I. The calculated σ_2 is shown in

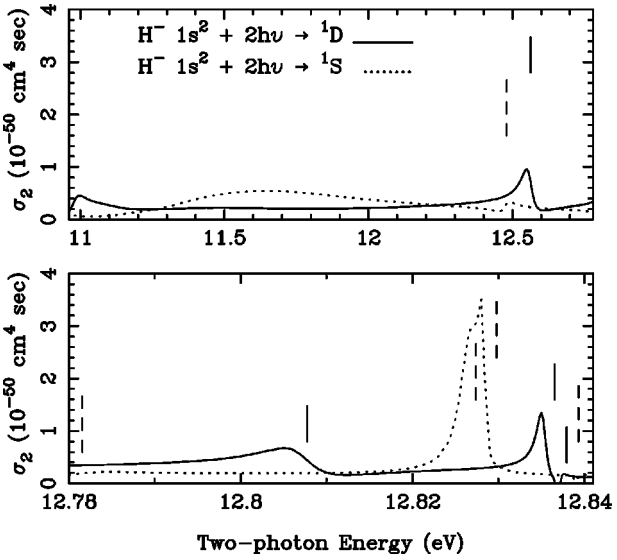

FIG. 4. TPDCS of H^- below the $n=3$ threshold of H. The vertical solid line marks the position of the ^1D resonances; the dashed line indicates the position of the ^1S resonances.

Fig. 4. Note that the scale for the abscissa of the lower panel is larger than that of the upper panel by a factor of 30. It is clear from this figure that for the resonances in this region, the TPDCS is even smaller than those below $n=2$. Hence, it would be more difficult to measure these resonances in a TPDCS experiment. In this figure, an interesting interference effect can be seen between the close-lying resonances such as $^1S(3)$ and $^1S(4)$ as well as $^1D(3)$ and $^1D(4)$. We also note that just above the $n=2$ threshold, there is a small but sharp ^1D TPDCS rise. It would be interesting to know whether this indicates the presence of a ^1D shape resonance.

In Table I, the mass polarization correction for the $^1D(1)$ and $^1S(3)$ states is larger than that of the other states below $n=3$; this indicates the presence of a larger $3p3p$ component in the wave function. Again using the single-particle picture discussed before, one can anticipate that the corresponding σ_2 and oscillator strengths will be larger. This is reflected in the spectra in Fig. 4. The TPDCS peaks for $^1D(1)$ and $^1D(3)$ appear to be of the same height; this is only because the width of $^1D(1)$ is 37 times that of $^1D(3)$.

The σ_2 for energies below the $n=3$ threshold has been calculated by Sánchez *et al.* [5], but only the lowest two ^1S and three ^1D resonances were reported. Their resonance energies agree reasonably well with the results in Table I. However, their line profiles are somewhat different from those of this work. The energies and widths in Table I also agree quite well with those of Pathak *et al.* [19].

In conclusion, we have performed a precision calculation for the TPDCS of H^- by means of a non-Hermitian Floquet theory using the saddle-point technique for resonance wave functions. To our knowledge, this is the first time that a fully correlated wave function has been used in such a Floquet matrix. We obtain the TPDCS by suppressing the single-photon detachment channel in the intermediate wave functions. It appears that our predicted ^1D resonance energy and width agree closely with the recent experiment [10]. Our predicted TPDCS peak is an *ab initio* theoretical result that is well within the experimental uncertainty. However, the error bar for this experimental data is quite large. We hope that a higher-precision experiment can be carried out in the future to reduce this error bar and to perform a TPDCS for higher prominent resonances. This would allow a more critical assessment of the present theory.

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