PHYSICAL REVIEW A VOLUME 46, NUMBER 5 1 SEPTEMBER 1992

# Two- and three-photon detachment of $H^-$ by a weak field

Daniel Proulx and Robin Shakeshaft
*Physics Department, University of Southern California, Los Angeles, California 90089-0484*
(Received 3 June 1992)

We describe a method for calculating rates for multiphoton detachment or ionization of a two-electron system by a perturbative field. We have applied the method to $H^-$, and we present estimates of two- and three-photon detachment rates. In particular, we explore the $^1S^e$ and $^1D^e$ Feshbach resonances below the $n = 2$ and $n = 3$ excitation thresholds of H; these resonances lie in the "excess-photon detachment" regime, where one photon is already sufficient to detach the electron.

PACS number(s): 32.80.Wr, 32.90.+a

Accurate rates for *multi*photon detachment of the negative hydrogen ion $H^-$ by a weak (perturbative) field have proved to be especially difficult to calculate. There are only a few published results of calculations taking the electron-electron interaction into full account (see, e.g., Refs. [1–5]), and there are significant discrepancies between these results (a comparison of different results is given in Ref. [4]). In this paper we describe a method for calculating rates for multiphoton detachment or ionization of a two-electron system by a perturbative field, and we present results of an application to $H^-$. We give rates for two- and three-photon detachment of $H^-$ by a linearly polarized field. In particular, we explore the region of the $^1S^e$ and $^1D^e$ Feshbach resonances below the first and second excitation thresholds of hydrogen. These resonances are reached by two photons and lie in the "excess-photon detachment" region where one photon is already sufficient to detach the electron [6,7]. In our calculations we employ a two-electron basis composed of products of one-electron complex radial Sturmian functions and spherical harmonics, and our results are, for most frequencies, fairly well converged with respect to increasing basis size.

Let $H_a$ be the Hamiltonian of the atomic system, and let $V_+e^{-i\omega t}+V_-e^{i\omega t}$ be the interaction of this system with a monochromatic classical field of frequency $\omega$, within the dipole approximation. If $E_i^{(0)}$ and $|\Psi_i\rangle$ denote the unperturbed initial energy and state vector, the amplitude for the system to absorb $N$ photons and undergo a transition to a state represented by $|\Psi_f^-\rangle$, with one electron in the continuum, is, within lowest (i.e., $N$th) -order perturbation theory,

$$A_{fi}^{(N)} = \langle\Psi_f^-|V_+|\mathcal{F}_{N-1}^{(N-1)}\rangle, \tag{1}$$

where the $N$th-order harmonic components $|\mathcal{F}_N^{(N)}\rangle$ satisfy the coupled (Dalgarno-Lewis) equations

$$(E_i^{(0)} + N\hbar\omega - H_a)|\mathcal{F}_N^{(N)}\rangle = V_+|\mathcal{F}_{N-1}^{(N-1)}\rangle, \quad N \geq 1, \tag{2}$$

$$|\mathcal{F}_0^{(0)}\rangle = |\Psi_i\rangle. \tag{3}$$

For simplicity, we neglect spin-orbit coupling so that we can factor the spin out of the problem. We denote the electron that is ejected as 1, and the electron that remains bound in the residual atomic system as 2. The final channel $f$ is specified by the parity, by the total orbital angular momentum and magnetic quantum numbers $L$ and $M$ of the two-electron system, by the individual orbital angular momentum quantum numbers, $l_1$ and $l_2$, of electrons 1 and 2, and by the (positive) energy $\varepsilon$ with which electron 1 emerges. Denoting the atomic number of the nucleus by $Z$, we subtract from the atomic potential acting upon electron 1 the Coulomb potential $-(Z-1)e^2/r_1$ due to the nucleus when it is screened by electron 2; the remaining potential acting upon electron 1 is $W \equiv e^2(1/r_{12} - 1/r_1)$, and this is "short" range. Speaking loosely, we refer to $W$ as the "final-state correlation" (FSC). If we were to neglect FSC, the final state would be represented by the direct product $|\psi_{l_1,\varepsilon}^-\rangle \otimes |\phi_{l_2}\rangle$, appropriately symmetrized and summed over individual magnetic quantum numbers, where $|\psi_{l_1,\varepsilon}^-\rangle$ represents electron 1 moving with energy $\varepsilon$ in the Coulomb potential $-(Z-1)e^2/r_1$ (note $Z = 1$ in the case of $H^-$) and where $|\phi_{l_2}\rangle$ represents electron 2 bound in the isolated residual system. Introducing the resolvent $G_a^{\pm}(E) = (E \pm i\eta - H_a)^{-1}$, where $\eta$ is positive but infinitesimal, and defining $E_f^{(0)} \equiv E_i^{(0)} + N\hbar\omega$, the exact final-state vector is given by the Lippmann-Schwinger equation:

$$|\Psi_f^-\rangle = \mathcal{P}\left(1 + G_a^-(E_f^{(0)})W\right)(|\psi_{l_1,\varepsilon}^-\rangle \otimes |\phi_{l_2}\rangle), \tag{4}$$

where $\mathcal{P}$ is the symmetrization [7] operator. Substituting the right-hand side of Eq. (4) into the right-hand side of Eq. (1), noting that $[G_a^-(E)W]^\dagger = WG_a^+(E)$ and that Eq. (2) implies that $G_a^+(E_f^{(0)})V_+|\mathcal{F}_{N-1}^{(N-1)}\rangle = |\mathcal{F}_N^{(N)}\rangle$, we obtain

$$A_{fi}^{(N)} = B_{fi}^{(N)} + C_{fi}^{(N)}, \tag{5a}$$

$$B_{fi}^{(N)} = \sqrt{2}(\langle\psi_{l_1,\varepsilon}^-| \otimes \langle\phi_{l_2}|)V_+|\mathcal{F}_{N-1}^{(N-1)}\rangle, \tag{5b}$$

$$C_{fi}^{(N)} = \sqrt{2}(\langle\psi_{l_1,\varepsilon}^-| \otimes \langle\phi_{l_2}|)W|\mathcal{F}_N^{(N)}\rangle. \tag{5c}$$

The quantity $B_{fi}^{(N)}$ is just the amplitude obtained when FSC is omitted, and $C_{fi}^{(N)}$ is the correction accounting for FSC. Writing $H_a \equiv H_0 + W$, and noting that $|\psi_{l_1,\varepsilon}^-\rangle \otimes |\phi_{l_2}\rangle$ is an eigenvector of $H_0$ with eigenvalue $E_f^{(0)}$, we can replace $W$ by $H_a - E_f^{(0)} + H_0^\dagger - H_0$ on the right-hand side

 ©1992 The American Physical Society

of Eq. (5c); using Eq. (2) we see that the part of $C_{fi}^{(N)}$ involving $H_a - E_f^{(0)}$ cancels with $B_{fi}^{(N)}$, and hence we can express $A_{fi}^{(N)}$ in the alternative forms

$$A_{fi}^{(N)} = \sqrt{2}(\langle\psi_{l_1,\varepsilon}^-| \otimes \langle\phi_{l_2}|)(H_0^\dagger - H_0)|\mathcal{F}_N^{(N)}\rangle \quad (6)$$

$$= \sqrt{2}(\langle\psi_{l_1,\varepsilon}^-| \otimes \langle\phi_{l_2}|)(E_f^{(0)} - H_0)|\mathcal{F}_N^{(N)}\rangle. \quad (7)$$

The last form, i.e., Eq. (7), is particularly suitable for computation since $H_0$ does not contain the electron-electron interaction (and therefore matrix elements of $H_0$ can be calculated easily and rapidly, with minimum roundoff error), but, of course, the harmonic component $|\mathcal{F}_N^{(N)}\rangle$ does contain the electron-electron interaction. More importantly, each of the three different expressions given by Eqs. (5)–(7) is exact and yet the final state is represented by the (symmetrized) direct product $|\psi_{l_1,\varepsilon}^-\rangle \otimes |\phi_{l_2}\rangle$, which has a simple closed-form expression in position space; this is a substantial simplification, for which we pay only a modest price, namely, rather than calculate $|\mathcal{F}_{N-1}^{(N-1)}\rangle$, as required by expression (1) for $A_{fi}^{(N)}$, we must calculate $|\mathcal{F}_N^{(N)}\rangle$. We note also that the form given by Eq. (6) holds for strong (nonperturbative) fields, and a form similar to this has been used as a starting point to calculate partial rates for ionization of atomic hydrogen by strong fields [8].

We solved Eq. (2) for the harmonic components on our two-electron basis; this basis consisted of terms $S_{nl}^{\kappa}(r_1)S_{n'l'}^{\kappa}(r_2)Y_{ll'}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$, where $Y_{ll'}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ couples spherical harmonics and where $S_{nl}^{\kappa}(r)$ is a radial Sturmian function which is a Laguerre polynomial in $\kappa r$ of degree $n_r \equiv n-l-1$ multiplied by $(\kappa r)^{l+1}e^{i\kappa r}$. We chose the "wave number" $\kappa$ to lie in the upper right quadrant of the complex $\kappa$ plane so as to simulate both outgoing-wave open channels and exponentially decaying closed channels [9]. (If $N$ is less than the minimum number $N_{\min}$ of photons which the ion must absorb to release an electron, $|\mathcal{F}_N^{(N)}\rangle$ has only closed channels, but if $N \geq N_{\min}$, then $|\mathcal{F}_N^{(N)}\rangle$ has both open and closed channels.) Our basis consisted of terms up to, at most, $l$, $l' \leq 3$ and $n_r$, $n_r' \leq 20$, and (depending on $\kappa$) gave an electron affinity of $H^-$ between 0.0274 and 0.0276 a.u., compared to the accurate (Pekeris) value 0.027 751 a.u. The results presented below were obtained using Eq. (7), but, as a check, we simultaneously calculated $A_{fi}^{(N)}$ according to Eq. (5) (and always obtained good agreement) [10]. We note that any estimate of $A_{fi}^{(N)}$ obtained by expansion on a discrete basis formally diverges, in some cases, as the number of radial basis functions increases, since the final wave function of the ejected electron is a standing wave, composed of both ingoing and outgoing waves, while a discrete basis can only simulate ingoing- *or* outgoing-wave boundary conditions (not both); this matter is discussed in Ref. [9], and as in that work we used Padé summation to analytically continue the divergent series. The required basis size increases significantly with an increase in the number of photons that are included, but is moderately insensitive to whether the frequency is below or above the threshold for excess-photon detachment, since in applying Eqs. (5)–(7) we must handle harmonic components having both open and closed channels even at frequencies below the excess-photon detachment threshold.

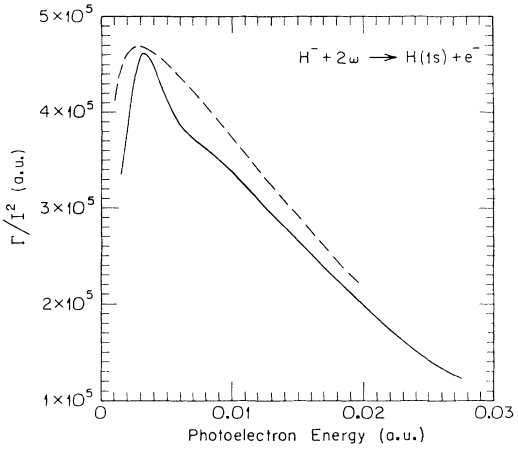


FIG. 1. Rate $\Gamma$, divided by the square of the intensity $I$, for two-photon detachment of $H^-$, with the H atom left in the ground state. Broken line, results of Liu, Gao, and Starace [4]; solid line, present results. Note $\Gamma/I^2$ is independent of $I$.

In Figs. 1 and 2 we show the total rates (integrated over angles) for two- and three-photon detachment of $H^-$ over the range of frequencies below the threshold for excess photon detachment. We compare our results with the semiempirical adiabatic hyperspherical results of Liu, Gao, and Starace [4]; the relative difference is 10% or less. As the photoelectron energy increases, the rate first rises due to the increase in available phase space, but the rate quickly reaches a maximum (long before the photoelectron energy reaches the electron affinity) and starts falling due to the difficulty the photoelectron has in acquiring momentum. Our results are not completely reliable for photoelectron energies below, and in the vicinity of, the maximum of the rate. As an independent check on the accuracy of our results we calculated the induced

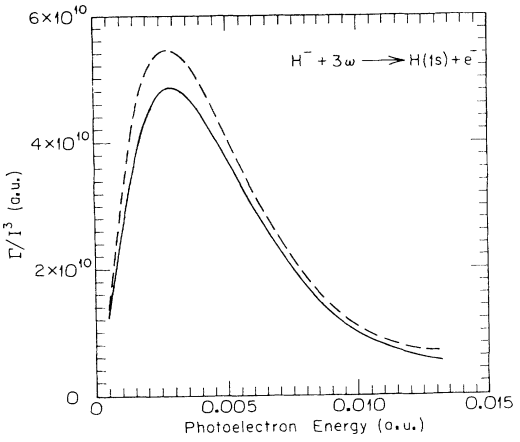


FIG. 2. Same as Fig. 1, but for three-photon detachment, with $\Gamma$ divided by $I^3$.

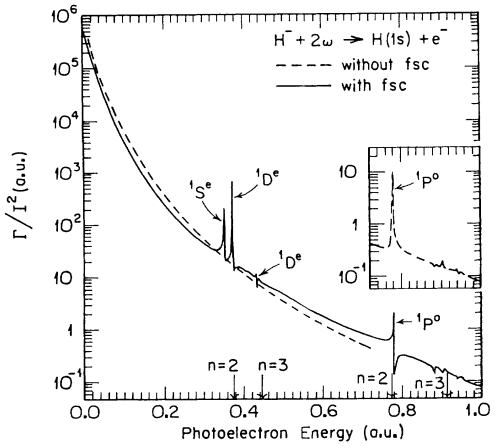


FIG. 3. Two-photon detachment in the excess-photon detachment region. The broken line shows results obtained when final-state correlation (FSC) is omitted.

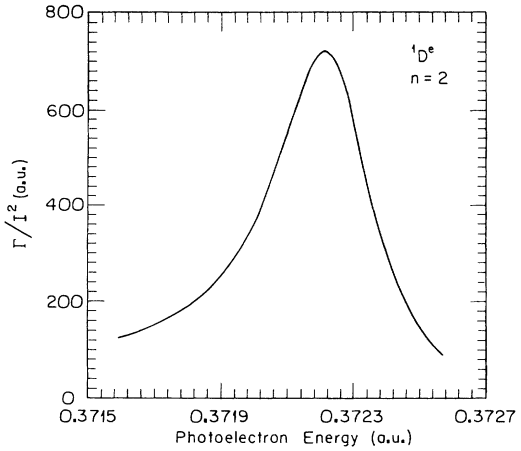


FIG. 5. $^1D^e$ resonance profile, below the $n = 2$ excitation threshold of H.

width of the ground-state level, which for frequencies below the threshold for excess photon detachment can be expressed as $-2\,\mathrm{Im}\langle \mathcal{F}_{N-1}^{(N-1)} | V_- | \mathcal{F}_N^{(N)} \rangle$ and should be identical to the total rate (multiplied by $\hbar$). In Tables I and II we compare the induced width with the rate calculated from Eq. (7).

In Fig. 3 we show the two-photon detachment rate over a wide range of frequencies above the threshold for excess-photon detachment. The rate falls rapidly as the photoelectron energy increases, but rises sharply at the $^1S^e$ and $^1D^e$ Feshbach resonances below the $n = 2$ and $n = 3$ excitation thresholds of H. These resonances are in the final state, and are not reproduced when FSC is neglected. At still higher photoelectron energies the $^1P^o$ shape resonance above the $n = 2$ excitation threshold is seen. This shape resonance occurs in an intermediate state, reached by absorption of the first photon; it appears even when FSC is neglected (since correlation is included in $|\mathcal{F}_1^{(1)}\rangle$), although the line shape is incorrect when FSC is omitted. We did not locate the $^1P^o$ Feshbach resonances below the $n = 2$ threshold, but we did reproduce these resonances in the one-photon detachment rate, in good agreement with earlier results [11].

In Figs. 4–6 we show in more detail the three prominent Feshbach resonances seen in Fig. 3. Since the $^1S^e$ and $^1D^e$ resonances below the $n = 2$ threshold are approximately symmetric, we can graphically deduce the widths of the profiles, and they are in good agreement with earlier calculated values [6]. The $^1D^e$ resonance below the $n = 3$ threshold is highly asymmetric; evidently there is strong interference with the two-photon detachment background.

Multiphoton detachment of $H^-$ has been observed [12], but not in the resonance region. (Moreover, rates were not measured, and the experiment was performed at pulse energies such that perturbation theory is probably unreliable.) Taking an "average" value of $100I^2$ a.u. for the two-photon rate in the resonance region below the $n = 2$ threshold, and noting that the one-photon rate in the same frequency range (i.e., $\omega \approx 5.4$ eV) is about $2I$ a.u., we obtain one- and two-photon rates of about

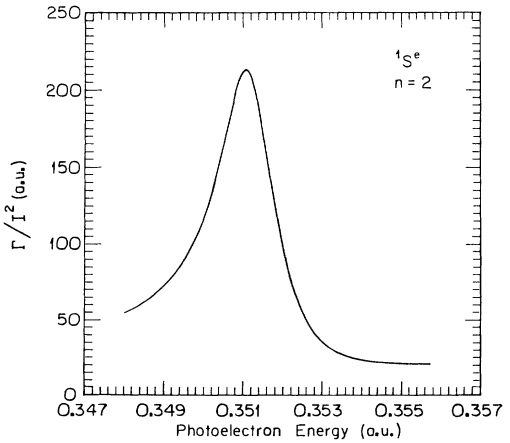


FIG. 4. $^1S^e$ resonance profile, below the $n = 2$ excitation threshold of H.

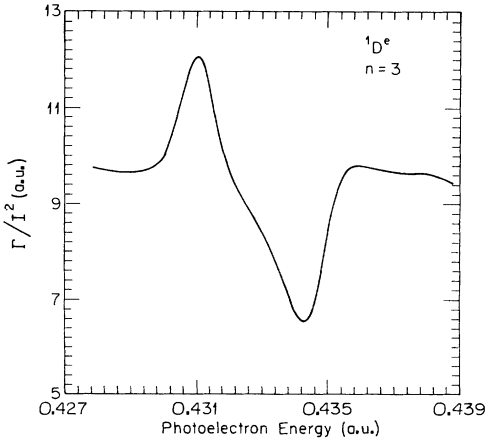


FIG. 6. $^1D^e$ resonance profile, below the $n = 3$ excitation threshold of H.

TABLE I. $\Gamma_a$ and $\Gamma_b$ are, respectively, the rates for two-photon detachment calculated from Eq.(7) and from the induced width of the ground-state level for various values of the photoelectron energy $\varepsilon$ and a basis $l, l' \leq 2$, $n_r, n_r' \leq 20$, $|\kappa| = 0.7$ and $\arg(\kappa) = 70°$. All quantities are in a.u.

| $\varepsilon$ | $\Gamma_a/(10^5 I^2)$ | $\Gamma_b/(10^5 I^2)$ |
|---|---|---|
| 0.001 | 3.558 | 4.340 |
| 0.005 | 4.087 | 4.066 |
| 0.010 | 3.324 | 3.317 |
| 0.015 | 2.609 | 2.588 |
| 0.020 | 1.951 | 1.944 |
| 0.025 | 1.432 | 1.431 |

$10^{12}$ and $10^9$ sec$^{-1}$, respectively, at an intensity $I$ of $10^{11}$ W/cm$^2$ [13]. Although the two-photon rate is several orders of magnitude below the one-photon rate, the one- and two-photon signals are well separated in energy (by about 5 eV) so that the two-photon resonances should be observable [14].

TABLE II. Same as Table I, but for three-photon detachment and a basis $l, l' \leq 3$, $n_r, n_r' \leq 20$, $|\kappa| = 0.5$ and $\arg(\kappa) = 70°$.

| $\varepsilon$ | $\Gamma_a/(10^{10} I^3)$ | $\Gamma_b/(10^{10} I^3)$ |
|---|---|---|
| 0.0015 | 3.764 | 4.908 |
| 0.0030 | 4.877 | 5.146 |
| 0.0050 | 3.741 | 3.988 |
| 0.0070 | 2.322 | 2.397 |
| 0.0085 | 1.516 | 1.574 |
| 0.0105 | 0.890 | 0.919 |

We thank T-N. Chang and R. M. Potvliege for very helpful discussions. We also thank C-R. Liu, B. Gao, and A. F. Starace for communicating their results to us prior to publication. One of us (D.P.) gratefully acknowledges support from the Natural Sciences and Engineering Research Council of Canada. This work was supported by the NSF under Grant No. PHY-9017079.

[1] M. G. Fink and P. Zoller, J. Phys. B **18**, L373 (1985).

[2] T. Mercouris and C. A. Nicolaides, J. Phys. B **21**, L285 (1988).

[3] M. Crance, J. Phys. B **23**, L285 (1990).

[4] C-R. Liu, B. Gao, and A. F. Starace (private communication).

[5] For a recent review of calculations of rates for one- and two-photon detachment of $H^-$ based on hyperspherical coordinates, see A. F. Starace (private communication).

[6] Line shapes of resonances of $H^-$ in the excess-photon detachment region have not previously been calculated. However, the positions and widths of these resonances have been calculated by, e.g., T. Scholz, P. Scott, and P. G. Burke, J. Phys. B **21**, L139 (1988); and A. K. Bhatia and Y. K. Ho, Phys. Rev. A **41**, 504 (1990), and references therein. We note also that line shapes of two-photon resonances of Al in the excess-photon ionization region have been recently calculated by F. Robicheaux and B. Gao, Phys. Rev. Lett. **67**, 3066 (1991).

[7] We have $\mathcal{P} \equiv [1+(-1)^S P]/\sqrt{2}$ where $P$ permutes the two electrons and where $S$ $(= 0, 1)$ is the total spin quantum number.

[8] R. M. Potvliege and R. Shakeshaft, Phys. Rev. A **41**, 1609 (1990); M. Dörr, D. Feldmann, R. M. Potvliege, H. Rottke, R. Shakeshaft, K. W. Welge, and B. Wolff-Rottke, J. Phys. B **25**, L275 (1992).

[9] M. Dörr, R. M. Potvliege, and R. Shakeshaft, J. Opt. Soc. Am. B **7**, 433 (1990).

[10] We used the velocity gauge. For large $N$, convergence of the $N$-photon amplitude $A_{fi}^{(N)}$ with respect to increasing basis size is more rapid in the velocity gauge than in the length gauge; this is due to the nature of the asymptotic boundary conditions of the harmonic components. See Ref. [9] above.

[11] J. T. Broad and W. P. Reinhardt, Phys. Rev. A **14**, 2159 (1976); H. R. Sadeghpour, C. H. Greene, and M. Cavagnero, Phys. Rev. A **45**, 1587 (1992).

[12] C. Y. Tang, P. G. Harris, A. H. Mohaghegi, H. C. Bryant, C. R. Quick, J. B. Donahue, R. A. Reeder, S. Cohen, W. W. Smith, and J. E. Stewart, Phys. Rev. A **39**, 6068 (1989).

[13] It is difficult to assess numerically the intensity at which perturbation theory breaks down, but it is probably higher than $10^{12}$ W/cm$^2$ in the frequency range 5–6 eV, except on resonance with a very long-lived state (i.e., a state with a very narrow width). In general, the radius of convergence of perturbation theory is determined by the distance from the origin of the nearest branch point singularity of the quasienergy in the complex field plane—see M. Pont and R. Shakeshaft, Phys. Rev. A **43**, 3764 (1991). Branch points correspond to either thresholds or discrete (bound or quasibound) states; the location of a branch point corresponding to a discrete state is determined by the size of the induced width relative to the Rabi frequency.

[14] Excess-photon detachment has been observed for $Cl^-$ by M. D. Davidson, H. G. Muller, and H. B. van Linden van den Heuvell, Phys. Rev. Lett. **67**, 1712 (1991) and for $Au^-$ by H. Stapelfeldt, P. Balling, C. Brink, and H. K. Haugen, Phys. Rev. Lett. **67**, 1731 (1991).