

## Multiphoton detachment, ionization, and simultaneous excitation of two-electron systems

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(Received 26 August 1993)

We present results of calculations of perturbative rates for two- and three-photon detachment and ionization of  $H^-$  and He, and for simultaneous excitation of  $H^-$ , by linearly polarized light over a range of frequencies extending into the “excess-photon detachment and ionization” region, a region replete with resonances. Simultaneous excitation of H is more probable than not in the case of two-photon detachment of  $H^-$ .

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

### I. INTRODUCTION

Recently we described a method for treating a two-electron system in a weak monochromatic radiation field, and we presented results of an application to two- and three-photon detachment of  $H^-$  and two-photon ionization of He [1, 2]. In this paper we present further results. The method is applicable to light of arbitrary polarization, but as in our previous calculations we restrict the polarization to linear.

We report, in particular, on three-photon detachment and ionization of  $H^-$  and He over a range of frequencies extending into the “excess-photon detachment and ionization” region where two photons are already sufficient to remove the electron—a region replete with resonances. In the case of  $H^-$ , the three-photon detachment cross section exhibits a prominent rise as the two-photon detachment threshold is crossed; we attribute this rise to the sharp rise in the two-photon detachment cross section, as explained further below. We also report on two-photon detachment of  $H^-$  accompanied by excitation of the residual H atom. We find that simultaneous excitation of the  $2p$  level of the H atom is significantly more probable than detachment without excitation once the frequency increases beyond the  $n = 2$  excitation threshold. The likelihood of simultaneous excitation is not surprising since one photon can eject one of the electrons, and the other photon can “almost” independently excite the remaining electron to the  $2p$  state; the energy mismatch for excitation is taken up by the free photoelectron, but as long as this energy mismatch is small the electron-electron correlation in the final state need not be strong. As the photon frequency approaches 0.375 a.u. the energy mismatch vanishes.

We begin, in the next section by reviewing the method. In Sec. III we present our results.

### II. METHOD

We denote by  $A_{fi}^{(N)}$  the lowest ( $N$ th) order amplitude for the atom to absorb  $N$  photons and undergo a transition from the initial unperturbed state  $i$ , in which both electrons are bound, to the final unperturbed state  $f$

in which one electron is bound and the other is free. If  $V(t) = V_+ e^{-i\omega t} + V_- e^{i\omega t}$  is the interaction of the atom with a monochromatic classical field of frequency  $\omega$ , within the dipole approximation, and if  $|\Psi_f^- \rangle$  represents the final state  $f$ , we have

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

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

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

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

where  $E_i$  and  $|\Psi_i \rangle$  are the energy and state vector of the atom in state  $i$ , and where  $H_a$  is the Hamiltonian of the atom. We now rearrange this expression for  $A_{fi}^{(N)}$  by first expressing  $H_a$  as

$$H_a \equiv H_0 + W, \quad (4)$$

where  $H_0$  is the *independent-particle* Hamiltonian that describes complete screening of the “outer” electron (the one which becomes free) by the “inner” electron (the one which remains bound). Thus if we label the outer and inner electrons by 1 and 2, respectively,  $W$  is the “short”-range potential  $W \equiv e^2(1/r_{12} - 1/r_1)$ , where  $r_{12}$  is the interelectron separation and where  $r_1$  is the distance of the outer electron from the nucleus. We neglect spin-orbit coupling so that we can factor the spin out of the problem. 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  $\epsilon$  with which electron 1 emerges. 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  $|\psi_{l_1, \epsilon}^- \rangle \otimes |\phi_{l_2} \rangle$ , appropriately symmetrized and summed over individual magnetic quantum numbers, where  $|\psi_{l_1, \epsilon}^- \rangle$  represents electron 1 moving with energy  $\epsilon$  in the Coulomb potential  $-e^2(Z-1)/r_1$  (with  $Z$  the atomic number of the system, e.g.,  $Z = 2$  for He) and where  $|\phi_{l_2} \rangle$  represents electron 2 bound in the iso-

lated residual  $\text{He}^+$  ion. Introducing the resolvent

$$G_a^\pm(E) = (E \pm i\eta - H_a)^{-1}, \quad (5)$$

where  $\eta$  is positive but infinitesimal, and defining  $E_f \equiv E_i + N\hbar\omega$ , the exact final-state vector is given by the Lippmann-Schwinger equation:

$$|\Psi_f^-\rangle = \mathcal{P}[1 + G_a^-(E_f)W](|\psi_{l_1,\epsilon}^-\rangle \otimes |\phi_{l_2}\rangle), \quad (6)$$

where  $\mathcal{P}$  is the symmetrization operator. Substituting the right-hand side of Eq. (6) into the right-hand side of Eq. (1), noting that  $[G_a^-(E)W]^\dagger = WG_a^+(E)$  and that Eq. (2) implies that  $G_a^+(E_f^{(0)})V_+|\mathcal{F}_{N-1}^{(N-1)}\rangle = |\mathcal{F}_N^{(N)}\rangle$ , yields

$$A_{fi}^{(N)} = B_{fi}^{(N)} + C_{fi}^{(N)}, \quad (7)$$

$$B_{fi}^{(N)} = \sqrt{2} \left( \langle \psi_{l_1,\epsilon}^- | \otimes \langle \phi_{l_2} | \right) V_+ |\mathcal{F}_{N-1}^{(N-1)}\rangle, \quad (8)$$

$$C_{fi}^{(N)} = \sqrt{2} \left( \langle \psi_{l_1,\epsilon}^- | \otimes \langle \phi_{l_2} | \right) W |\mathcal{F}_N^{(N)}\rangle. \quad (9)$$

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  $|\psi_{l_1,\epsilon}^-\rangle \otimes |\phi_{l_2}\rangle$  is an eigenvector of  $H_0$  with eigenvalue  $E_f^{(0)}$ , we can replace  $W$  by  $H_a - E_f + H_0^\dagger - H_0$  on the right-hand side of Eq. (9); 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  $A_{fi}^{(N)}$  as

$$A_{fi}^{(N)} = \sqrt{2} \left( \langle \psi_{l_1,\epsilon}^- | \otimes \langle \phi_{l_2} | \right) (H_0^\dagger - H_0) |\mathcal{F}_N^{(N)}\rangle \quad (10)$$

$$= \sqrt{2} \left( \langle \psi_{l_1,\epsilon}^- | \otimes \langle \phi_{l_2} | \right) (E_f^{(0)} - H_0) |\mathcal{F}_N^{(N)}\rangle. \quad (11)$$

The last form, i.e., Eq. (11), 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. Note, further, that Eq. (11) is exact and yet the final state is represented by the (symmetrized) direct product  $|\psi_{l_1,\epsilon}^-\rangle \otimes |\phi_{l_2}\rangle$ , 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 solved Eq. (2) for the harmonic components on a two-electron basis consisting of terms  $S_{n_l}^\kappa(r_1)S_{n_l'}^\kappa(r_2)Y_{ll'}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ , where  $Y_{ll'}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$  couples spherical harmonics and where  $S_{n_l}^\kappa(r)$  is a radial Sturmian function, with the “wave number”  $\kappa$  chosen 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 [3, 4]. The results presented below were obtained using Eq. (11), within the velocity gauge. The expansion of  $A_{fi}^{(N)}$  on a discrete basis formally diverges, as discussed earlier [5, 3, 4], and we summed the expansion using Padé extrapolation.

The basis that we use has several merits: (i) All matrix elements (of intra-atomic potentials and the atom-field interaction) can be evaluated in closed form. (ii) The matrix representations of the atom-field interaction and all other interactions except the electron-electron interaction are sparse (i.e., tridiagonal matrices, or products of tridiagonal matrices). (iii) The basis is discrete and complete (but see below). (iv) Nonspherically symmetric states can be easily described. However, our basis has several significant drawbacks: (i) Electron-electron correlation is not explicitly incorporated, and therefore estimates of most physical quantities converge rather slowly with increasing basis size. (ii) When the residual atom or ion is left in an excited (degenerate) state, the outgoing photoelectron experiences a long-range dipole interaction. This modifies the boundary conditions (see, e.g., Refs. [6] and [7]), and a large basis is required to incorporate this interaction. (iii) The three-body Coulomb interaction leads to logarithmic singularities in the wave function [8], and while they do not have a very significant effect, they cannot be described by our basis. (iv) While all matrix elements can be evaluated in closed form, round-off error can rapidly accumulate in the matrix elements of the electron-electron interaction if special care is not taken.

### III. RESULTS

Most of our results pertain to  $\text{H}^-$ , and we discuss these first. Recall that the polarization of the light is linear. In Figs. 1 and 2 we show total rates (integrated over all angles) for two- and three-photon detachment of  $\text{H}^-$ , with the residual H atom left in the ground state. We also

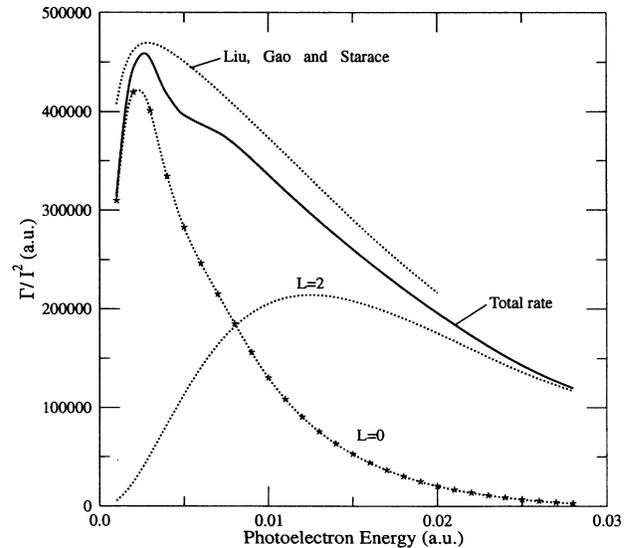


FIG. 1. Rate  $\Gamma$ , divided by the square of the intensity  $I$ , for two-photon detachment of  $\text{H}^-$ , with the H atom left in the ground state. We show both our estimates of the total two-photon rate and those of Liu *et al.* [9]. (Note  $\Gamma/I^2$  is independent of  $I$ .) The broken lines are the contributions to the total two-photon rate from the  $L = 0$  and  $L = 2$  partial waves.

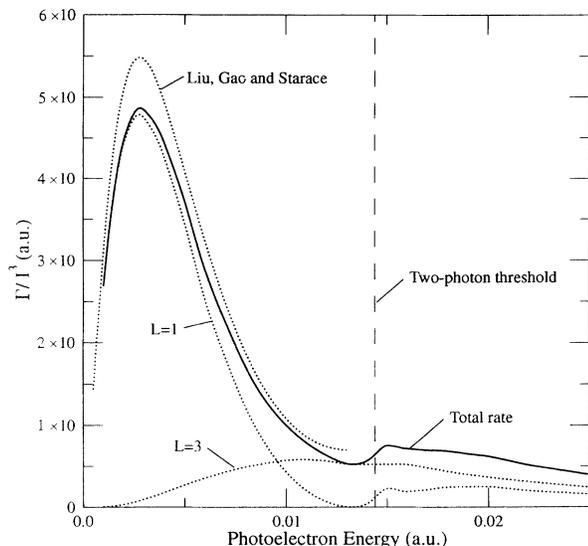


FIG. 2. Same as Fig. 1, but for three-photon detachment, with  $\Gamma$  divided by  $I^3$ .

give the contributions from the two partial waves (the  $L = 0$  and  $L = 2$  waves for the two-photon process and the  $L = 1$  and  $L = 3$  waves for the three-photon process). Where comparison is possible, namely 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 [9]; the relative difference is 10% or less. Our results are not completely reliable for photoelectron energies below, and in the vicinity of, the maximum of the total rate. Note that both the two- and three-photon detachment rates rise sharply as the photoelectron energy increases from zero. This is due to the increase in available phase space, and, as expected from the Wigner threshold law, the main contribution just above the threshold comes from the partial wave with the smallest value of  $L$ ; the angular momentum barrier precludes the emission of photoelectrons with linear momentum much less than  $(L + \frac{1}{2})$  a.u.

One expects the detachment rates to fall once the photoelectron energy increases beyond the electron affinity, since the linear momentum of the photoelectron then exceeds the characteristic atomic orbital momentum of the electron in its initial bound state. (Photons cannot impart linear momentum to the electron—at least within the dipole approximation—and so the photoelectron can acquire a linear momentum larger than the characteristic atomic orbital momentum only by absorbing photons while very close to the nucleus, which is improbable.) It is remarkable, however, that the two- and three-photon total detachment rates begin falling long before the photoelectron energy reaches the electron affinity (which is about 0.028 a.u.). This is in contrast to the case of one-photon detachment, where the rate does reach a maximum at approximately where the photoelectron energy and electron affinity are equal [10]. The onset of the decline in the two- and three-photon total detachment rates

at a photoelectron energy so close to threshold may be understood with reference to a propensity rule discussed in detail by Fano [11]. This rule states that the photoelectron absorbs preferentially the maximum angular momentum, if the photoelectron has an energy moderately far above threshold. (Roughly speaking, the rule follows from the fact that, as long as the active electron absorbs photons at a distance from the nucleus that is comparable to the characteristic binding radius, the angular momentum of the photoelectron increases with its linear momentum, and therefore with its energy.) Thus, while the contribution from the partial wave with the smallest  $L$  rises sharply just above threshold, this contribution reaches a maximum, and it subsequently declines rapidly, at photoelectron energies not far above the threshold; this drop is not fully offset by the rising contribution from the partial wave with the largest  $L$ , so that the total rate begins declining long before the photoelectron energy exceeds the electron affinity.

The vertical broken line in Fig. 2 marks the threshold for two-photon detachment. We see that the three-photon detachment rate rises at this threshold. A similar feature was *not* seen in the two-photon detachment rate at the one-photon detachment threshold [1]. The rise in the three-photon detachment rate at the two-photon detachment threshold is due to a rise in the contribution from the  $L = 1$  partial wave, and we believe that this originates in a (coherent) two-step process whereby the ion first absorbs two photons, without  $L$  changing (i.e.,  $L$  remains zero), followed by the absorption of another photon which puts the ion into a  $L = 1$  partial wave. The first leg of the process is enhanced by the sharp rise in the  $L = 0$  contribution to the two-photon detachment rate seen in Fig. 1 at low photoelectron energies, and this results in the enhancement of the  $L = 1$  contribution to the three-photon detachment rate at the two-photon detachment threshold. As mentioned above, the one-photon detachment rate reaches a maximum quite far above threshold, so a rise in the two-photon detachment rate at the one-photon detachment threshold is not expected.

Previously we showed profiles of several resonances in the two-photon detachment rate (they occur at frequencies above the threshold for excess photon detachment) [1]. In particular, the two-photon detachment rate has  $^1S^e$  and  $^1D^e$  Feshbach resonances below the  $n = 3$  threshold, and we show the lowest of these in Fig. 3. These resonances combine to give a highly asymmetric profile, which has a slight inflection. Previously [1] we overlooked the inflection and we misidentified the single (combined) profile as a pure  $^1D^e$  resonance profile whose asymmetry was incorrectly attributed to strong interference with the two-photon detachment background.

In Fig. 4 we show rates for two-photon detachment of  $H^-$ , including simultaneous excitation to the  $2s$  or  $2p$  state of the residual H atom. We cover a range of photoelectron energies up to, and slightly beyond, where one photon can excite the  $^1P^o$  shape resonance (i.e., above the threshold for one-photon excitation of the  $n = 2$  levels of H). We have not attempted to calculate the resonance structures to very high accuracy since we are primarily interested in illustrating qualitative features. As

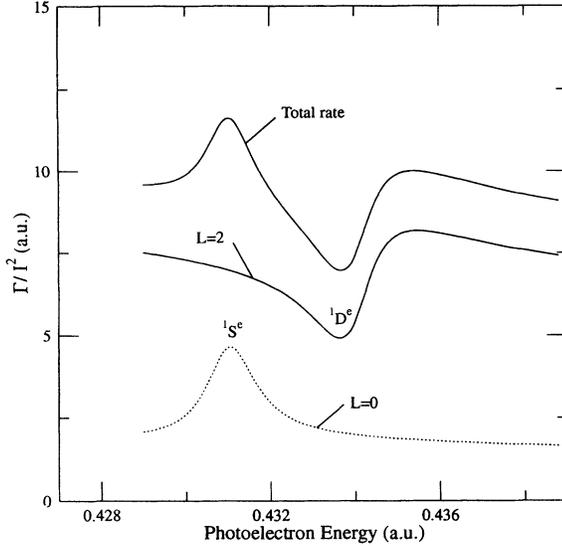


FIG. 3. Resonance structure in the rate for two-photon detachment of  $H^-$  due to the lowest  $1S^e$  and  $1D^e$  resonances below the  $n = 3$  threshold.

mentioned in the Introduction, we can view simultaneous excitation to the  $2p$  state as a process in which one of the photons ejects one electron, and the other photon excites, more or less independently, the remaining bound electron from the  $1s$  to the  $2p$  state of  $H$ . The energy mismatch for excitation, which vanishes when the photon energy equals  $0.375$  a.u., is taken up by the free photoelectron, but *no orbital angular momentum need be exchanged* between the two electrons. Simultaneous

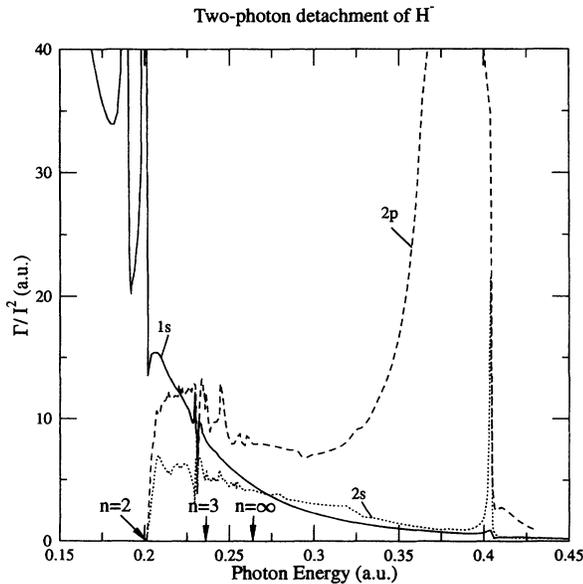


FIG. 4. Rates for two-photon ionization of  $H^-$ , including simultaneous excitation to the  $2s$  or  $2p$  states. ( $\Gamma$  is divided by  $I^2$ .) The arrows mark the thresholds for excitation of the  $n = 2$  and  $n = 3$  levels of  $H$ , and the threshold for double escape.

excitation to the  $2p$  state is more probable than detachment without excitation because (i) as long as the energy mismatch for excitation to the  $2p$  state is small, electron-electron correlation in the final state can be weak, and (ii) the promotion of the bound electron to an excited state enables the free photoelectron to emerge with less kinetic energy, and therefore with less linear momentum, than it would otherwise have. (Recall that photons cannot transfer linear momentum.) Indeed we see that the rate for simultaneous excitation of the  $2p$  level rises sharply just above the  $n = 2$  excitation threshold, drops a little at higher photon energies, and then rises steeply again as the photon energy approaches  $0.375$  a.u., at which point the  $1s$ - $2p$  one-photon transition in  $H$  becomes resonant. In contrast, the rate for detachment without excitation declines rapidly as the photon energy increases (except near resonances).

Simultaneous excitation to the  $2s$  state is much less probable than simultaneous excitation to the  $2p$  state since the remaining bound electron cannot be promoted from the  $1s$  to the  $2s$  state of  $H$  by one photon alone; the two electrons must simultaneously exchange orbital angular momentum. The rate for simultaneous excitation of the  $2s$  state does rise sharply just above the  $n = 2$  excitation threshold, but it subsequently declines until the photon energy reaches about  $0.4$  a.u. where the rate is substantially enhanced by one-photon excitation to the  $1P^o$  shape resonance. (The effect of the  $1P^o$  shape resonance on simultaneous excitation of the  $2p$  state is dwarfed by the near resonance of the  $1s$ - $2p$  one-photon transition in  $H$ .)

We now give a brief mathematical description of the large peak in the amplitude for two-photon detachment of  $H^-$  with simultaneous excitation to the  $2p$  state of the core (i.e., the  $H$  atom) when the frequency is on resonance with the  $1s$ - $2p$  transition in the core. Let us denote the amplitude for simultaneous excitation to the  $nl$  state of the core as  $A_{\mathbf{k},nl}^{(2)}$  where  $\hbar\mathbf{k}$  is the final momentum of the free photoelectron,  $\mu$  is its mass, and  $\epsilon \equiv \hbar^2 k^2 / (2\mu)$  is its energy. Let  $|\Psi_{\mathbf{k},nl}^-\rangle$  represent the (continuum) state of  $H^-$  in which, at asymptotically large distances, one electron moves with momentum  $\hbar\mathbf{k}$  and the other electron is bound in the  $nl$  state of the core. Thus  $|\Psi_{\mathbf{k},nl}^-\rangle$  is the (exact) eigenvector of the atomic Hamiltonian  $H_a$  with eigenvalue  $E_{knl} \equiv \hbar^2 k^2 / (2\mu) - e^2 / (2n^2 a_0)$ . We have

$$A_{\mathbf{k},nl}^{(2)} = \langle \Psi_{\mathbf{k},nl}^- | V_+ G_a^+(E_i + \hbar\omega) V_+ | \Psi_i \rangle. \quad (12)$$

The spectral decomposition of  $G_a(E)$  is

$$G_a^+(E) = \frac{|\Psi_i\rangle\langle\Psi_i|}{E - E_i} + \sum_{n',l'} \int d^3k' \frac{|\Psi_{\mathbf{k}',n'l'}^-\rangle\langle\Psi_{\mathbf{k}',n'l'}^-|}{E - E_{k'n'l'}}, \quad (13)$$

where  $E_i$  is the ground-state energy of  $H^-$ . It should be understood that the sum over  $n'$  and  $l'$  on the right-hand side of Eq. (13) also includes an integration over the continuum states of the core. Inserting the spectral decomposition of  $G_a(E_i + \hbar\omega)$  into Eq. (12), noting that  $\langle\Psi_i|V_+|\Psi_i\rangle = 0$ , and using energy conservation (for a

two-photon transition) to write  $E_i + \hbar\omega = E_{knl} - \hbar\omega$ , gives

$$A_{\mathbf{k},nl}^{(2)} = \sum_{n',l'} \int d^3k' \frac{\langle \Psi_{\mathbf{k},nl}^- | V_+ | \Psi_{\mathbf{k}',n'l'}^- \rangle \langle \Psi_{\mathbf{k}',n'l'}^- | V_+ | \Psi_i \rangle}{E_{knl} - \hbar\omega - E_{k'n'l'}}. \quad (14)$$

If the states  $nl$  and  $n'l'$  are low-lying bound states of the core, and if a dipole transition between these states is allowed, the matrix element  $\langle \Psi_{\mathbf{k},nl}^- | V_+ | \Psi_{\mathbf{k}',n'l'}^- \rangle$  is maximum when  $\mathbf{k} = \mathbf{k}'$ ; this is the basis of the isolated core excitation technique so commonly used in experiments addressing multiphoton excitation of autoionizing states in multielectron atoms [12]. Suppose that the frequency  $\omega$  is on resonance with a particular dipole-allowed core transition  $n''l'' \rightarrow nl$ . In this case  $E_{knl} - E_{kn''l''} = \hbar\omega$ , and hence the energy denominator in the integrand on the right-hand side of Eq. (14) vanishes when  $k' = k$ , for  $n'l' = n''l''$ . Recalling that the matrix element  $\langle \Psi_{\mathbf{k},nl}^- | V_+ | \Psi_{\mathbf{k}',n''l''}^- \rangle$  is maximum when  $\mathbf{k} = \mathbf{k}'$  it follows that as long as the probability for one photon to detach an electron from  $\text{H}^-$ , and leave the core in the state  $n''l''$ , is significant, so that the matrix element  $\langle \Psi_{\mathbf{k}',n''l''}^- | V_+ | \Psi_i \rangle$  is appreciable, the two-photon amplitude  $A_{\mathbf{k},nl}^{(2)}$  strongly peaks for  $\omega$  on resonance with the subsequent dipole-allowed core transition. In fact, if correlation, i.e., if  $W$  (but not screening), were neglected in the continuum states of  $\text{H}^-$  (at least those states for which  $\mathbf{k}'$  is in the neighborhood of  $\mathbf{k}$ ), the amplitude  $A_{\mathbf{k},nl}^{(2)}$  would become *infinite* on resonance; this follows because the eigenvectors  $|\Psi_{\mathbf{k},nl}^- \rangle$  and  $|\Psi_{\mathbf{k}',n''l''}^- \rangle$  would each reduce to a direct product of a plane wave vector and a hydrogen atom bound state vector, and the matrix element  $\langle \Psi_{\mathbf{k},nl}^- | V_+ | \Psi_{\mathbf{k}',n''l''}^- \rangle$  would be proportional to the delta function  $\delta^3(\mathbf{k}' - \mathbf{k})$ , plus a finite correction, so the vanishing of the energy denominator would not be smoothed out by the integration over  $\mathbf{k}'$ .

If, in the final state, the correlation strength (energy) is  $\Delta E_{\text{corr}}$ , the time interval,  $\Delta t_{\text{corr}}$ , over which correlation can be neglected is  $\Delta t_{\text{corr}} \approx \hbar/\Delta E_{\text{corr}}$ . Thus correlation can be neglected in the final state only if the duration of the light pulse, and hence the coherence time of the light,  $\Delta t_{\text{coh}}$ , is shorter than  $\Delta t_{\text{corr}}$ ; but then the energy bandwidth,  $\hbar\Delta\omega$ , would be larger than  $\Delta E_{\text{corr}}$ , i.e., the uncertainty in the energy denominator on the right-hand side of Eq. (14) would be larger than  $\Delta E_{\text{corr}}$ . In writing down Eq. (12) we have assumed  $\Delta t_{\text{coh}}$  to be longer than all other relevant time scales. If, however, the two photons were temporally separated, the two-photon process would be incoherent, and in fact would be truly a sequential process in which the first photon photodetaches an electron, leaving the core in the ground state, and the second photon excites the core; the two-photon amplitude would become a product of two amplitudes, with one amplitude describing photodetachment and the other amplitude describing core excitation.

We remark, incidentally, that the cross section for one-photon detachment with simultaneous excitation to the  $2p$  level also exceeds the cross section for one-photon detachment without excitation [6, 7], at least not far above

the  $n = 2$  excitation threshold. However, this is due to the  $1P^o$  shape resonance just above the  $n = 2$  excitation threshold, which prefers to decay to the  $2s$  and  $2p$  states rather than to the  $1s$  state of  $\text{H}$ . Simultaneous photodetachment and excitation by one photon becomes less probable as the photon energy continues to increase, beyond the  $1P^o$  shape resonance.

Below the threshold for double escape, we see various structures in Fig. 4. These structures arise from two-photon excitation of Feshbach resonances below various excitation thresholds. (As noted above, we have not attempted to calculate these resonance structures to high accuracy. Nor have we attempted to search for finer structure, e.g., Galitis-Damburg oscillations [13, 6] above excitation thresholds.) Liu *et al.* [6] have calculated rates for two-photon detachment with simultaneous excitation to the  $2s$  and  $2p$  states for photoelectron energies up to about 0.29 a.u. (5 eV), but they found no resonance structures; the reason is that they did not include coupling to channels above the  $2s$  and  $2p$  channels, and therefore could not account for Feshbach resonances below the  $n = 3, 4, \dots$ , and higher channels. Liu *et al.* [6] were primarily interested in two-photon detachment with simultaneous excitation at photon energies just above the  $2s$ ,  $2p$  excitation thresholds (i.e., photon energies not much larger than 0.19 a.u.) and in this energy range their calculations are presumably accurate. On the other hand, our focus is not on the threshold region (in fact, we experience convergence difficulties very close to thresholds) but rather the region of somewhat higher photon energies where the coupling to higher channels is very important. Indeed, whereas we find simultaneous excitation to the  $2p$  state to be far more probable than simultaneous excitation to the  $2s$  state at higher photon energies, Liu *et al.* [6] find the reverse.

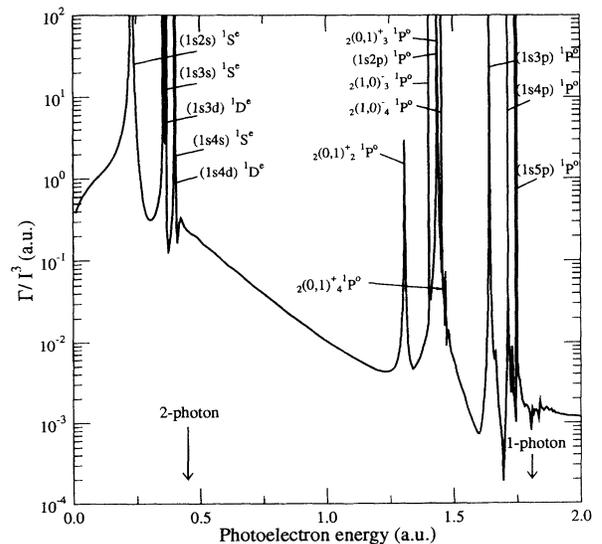


FIG. 5. Rate  $\Gamma$ , divided by the square of the intensity  $I$ , for three-photon ionization from the ground state of  $\text{He}$ , with the  $\text{He}^+$  ion left in the ground state. The arrows mark the thresholds for two- and one-photon ionization.

At a photon energy above about 0.2638 a.u. both electrons can be liberated by two photons, and we expect double escape to become the most probable process at photon energies higher than 0.5 a.u. since then the two electrons can escape without interacting whatsoever, and they can each depart with less linear momentum than one electron could do if the other one remained bound.

Finally, we turn to He. In Fig. 5 we show total rates (integrated over all angles) for three-photon ionization of the ground state of He by linearly polarized light over a range of frequencies extending from below to above the threshold for two-photon ionization. This region is very rich in structure, arising from resonances due to two-photon transitions to singly excited bound states (below the two-photon ionization threshold), three-photon transitions to doubly excited autoionizing states (below the

$n = 2$  and  $n = 3$  excitation thresholds of  $\text{He}^+$ ), and one-photon transitions to singly excited bound states (below the one-photon ionization threshold). We have labeled these resonances using the  $K$  and  $T$  quantum numbers of Herrick and Sinanoglu [14, 15].

#### ACKNOWLEDGMENTS

We thank Professor P. D. Burrow for drawing our attention to the inflection in the combined  $^1S^e$  and  $^1D^e$  resonance profile for  $\text{H}^-$  below the  $n = 3$  threshold. This work was supported by the National Science Foundation under Grant No. PHY-9017079. One of us (D.P.) gratefully acknowledges financial support from the Natural Sciences and Engineering Research Council of Canada.

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