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DOI

[10.1103/PhysRevA.50.2508](https://doi.org/10.1103/PhysRevA.50.2508)

Publication date

1994

Published in

Physical Review A

[Link to publication](#)

Citation for published version (APA):

van der Hart, H. W. (1994). Partial and total multiphoton detachment rates for H⁻ in a perturbative B-spline-based approach. *Physical Review A*, 50(3), 2508-2516.
<https://doi.org/10.1103/PhysRevA.50.2508>

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Partial and total multiphoton detachment rates for H^- in a perturbative B -spline-based approach

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(Received 19 July 1993; revised manuscript received 18 April 1994)

An *ab initio* approach has been applied to study multiphoton detachment rates for the negative hydrogen ion in the lowest nonvanishing order of perturbation theory. The approach is based on the use of B splines allowing an accurate treatment of the electronic repulsion. Total detachment rates have been determined for two- to six-photon processes as well as partial rates for detachment into the different final symmetries. It is shown that B -spline expansions can yield accurate continuum and bound-state wave functions in a very simple manner. The calculated total rates for two- and three-photon detachment are in good agreement with other perturbative calculations. For more than three-photon detachment little information has been available before now. While the total cross sections show little structure, a fair amount of structure is predicted in the partial cross sections. In the two-photon process, it is shown that the detached electrons mainly have s character. For four- and six-photon processes, the contribution from the d channel is the most important. For three- and five-photon processes p electrons dominate the electron emission spectrum. Detachment rates for s and p electrons show minima as a function of photon energy.

PACS number(s): 32.80.Wr

I. INTRODUCTION

For the practitioners of atomic-structure calculations it is a challenge to determine the properties of negative ions since the additional electron is bound primarily because of electron-electron correlations. Since the binding in negative ions approximately falls off as r^{-4} and is considerably weaker than the Coulomb potential in neutral or positive systems, the electron affinity generally is quite small and extensive calculations are required to obtain accurate electron affinities. An instructive example of the difficulties present in determining electron affinities is provided by the stable negative calcium ion, Ca^- , whose existence was established only a few years ago [1,2]. Only very recently, good agreement between the latest experimental value [3] and theory has been obtained after inclusion of the dielectronic core-valence polarization, which was found to decrease the theoretical electron affinity by a factor of 3 [4].

From an experimental point of view, negative ions are very interesting because the binding potential is so weak that, generally, only one bound state can exist. Since the binding potential of a negative ion falls off more rapidly than the binding potential of neutral and positive ions, the behavior of negative ions in laser fields can differ significantly from the behavior of neutral atoms.

The first multiphoton experiment on a negative ion, I^- , was reported by Hall *et al.* [5] already more than two decades ago, while in the past few years interest has been renewed. This has been caused by the development of new instrumental equipment and techniques, such as ion beams with sufficient densities and ion traps, and various groups have now determined absolute multiphoton detachment cross sections for a wide variety of negative

ions [6–10], mainly for the negative halide ions. Also very interesting is the observation of excess-photon detachment in which more photons than necessary for detachment are absorbed [11–13]. Angular distributions of electrons emitted in three-, four-, and five-photon detachment have been obtained for F^- by Blondel *et al.* [11]. However, for the most simple negative ion, H^- , experimental data is much more scarce [14–16]. For a recent review of experiments involving negative ions, see [17].

From a theoretical point of view, the situation is radically different. Much work has been done for H^- and much less for the heavier systems. Considering the latter first, Robinson and Geltman [18] performed the first calculation of multiphoton detachment rates in response to the experiments by Hall *et al.* [5]. More recently, for the negative halide ions, Crance [19] has determined multiphoton detachment rates using a frozen-core Hartree-Fock model approach. Jiang and Starace [20] have investigated two-photon detachment from Cl^- , while Pan *et al.* [21] have studied two-photon detachment from F^- to examine the effects of electron correlation. Two-photon detachment of I^- has been analyzed by L'Huillier and Wendin [22] to investigate many-body screening effects.

In contrast, there is a considerable amount of theoretical work for the negative hydrogen ion; see, for example, [23–30]. It is the simplest negative ion and it is a two-electron system. In determining multiphoton detachment cross sections, most theoretical work has so far been performed using a model potential approach, in which a potential is fitted to reproduce the known ground state energy and the ion is treated as a one-electron problem. The model potentials used to describe H^- usually consist of a δ -function zero-range potential or a potential which resembles a zero-range potential [23,24].

However, as already noted, electron-electron correla-

tions are essential for the binding of the additional electron and their effects have to be included in order to have a realistic description of the negative hydrogen ion. The effect of correlation manifests itself not only for the $1S^e$ ground state, but also the $1S^e$ continuum states are affected, while continuum states for other symmetries are affected much less. Because the model potential is fitted, the ground state energy is good, but, on the other hand, it is very difficult to obtain accurate continuum wave functions with such a method since this requires a good description of the correlated interactions in the region near the nucleus, where photons can be absorbed. However, in the length gauge, it is only required to obtain the correct phase shift of the continuum wave function to obtain good cross sections.

Despite this, only a few calculations of multiphoton detachment rates have been performed which explicitly include electron-electron correlation [25–30]. Fink and Zoller [25] used a hyperspherical approach to determine one- and two-photon detachment rates. Mercouris and Nicolaides [27,28] applied their many-electron many-photon approach to study two- to four-photon detachment. Proulx and Shakeshaft [29], using a Sturmian basis expansion, and Liu *et al.* [30] who used various model potentials and hyperspherical approaches, have determined cross sections for two- and three-photon detachment, whereas Crance [26] has determined rates for two- to five-photon detachment using a Slater-type basis. The only calculation in which excess-photon detachment rates were obtained was the one performed by Proulx and Shakeshaft [29], who were interested in the effects of doubly-excited resonances on the detachment rates.

It has been shown [4,31] that correlation in negative ions can be determined with high accuracy using B -spline-based basis sets. The reason for this is that the effects due to the continuum can be taken into account by a B -spline description. It is also possible to describe continuum wave functions accurately using B -spline basis sets [32–34]. Since basis functions can be constructed appropriate for both types of problems, a B -spline approach to the determination of partial and total multiphoton detachment rates in the lowest nonvanishing order of perturbation theory has been developed in which correlation effects are fully taken into account. B splines have already been used in the determination of multiphoton ionization cross sections [35–38]. Tang *et al.* [36] have applied B splines in a nonperturbative study of multiphoton processes including above threshold ionization in intense fields created by short laser pulses in neutral hydrogen. Tang *et al.* [35], Chang and Tang [37], and Tang and Bachau [38] have calculated multiphoton ionization spectra of the magnesium ion including angular distributions. The basis set they used consisted of configurations of one electron in an orbital with $n \leq 5$ and the other electron in a B -spline series with fixed angular momentum. Due to the magnitude of the correlations in H^- , demonstrated by significant contributions to the ground state energy from configurations with two continuum electrons [31], this approach is not readily suited for negative ions.

In this paper, we present a study of multiphoton de-

tachment rates of a negative ion using B splines. The approach to this problem is discussed in Sec. II: two different B -spline basis sets are combined, one basis set describing correlation effects and the other describing the continuum wave functions. The results obtained are given and discussed in Sec. III together with a comparison with other results. We present total as well as partial multiphoton detachment rates. The partial rates are of interest since from the relative intensity of the partial detachment spectra, the angular distributions of the emitted electrons can be derived.

II. THEORETICAL METHOD

The N -photon detachment rates divided by the laser intensity to the power N are determined in atomic units in the lowest-order perturbation approach [39], using the expression

$$\Gamma_N = 2\pi(2\pi\alpha)^N |M_{fi}^N|^2, \quad (1)$$

with the matrix element M_{fi}^N for N -photon transitions in the length formulation of the dipole operator between an initial state ψ_i with energy E_i and final state ψ_f with energy E_f given by

$$M_{fi}^N = \sum \frac{\langle \psi_f | r | \psi_{N-1} \rangle \cdots \langle \psi_1 | r | \psi_i \rangle}{[E_f - E_i - (N-1)\omega] \cdots [E_f - E_i - \omega]} \quad (2)$$

in which the frequency ω , because of energy conservation, is given by

$$\omega = \frac{E_f - E_i}{N} \quad (3)$$

and $|\psi_M\rangle$ denotes an intermediate state after absorption of M photons, $M = 1, \dots, N-1$. The summation in (2) is over all intermediate states $|\psi_M\rangle$. Partial detachment rates are obtained by considering each final angular momentum separately. The total rate is obtained by adding the partial rates. Since the rates are determined at a particular set of energies, different for each final angular momentum, a fit procedure is used to obtain the detachment rates at all energies.

To determine the N -photon detachment rates and cross sections for H^- by this perturbative method, an accurate description of all wave functions with total angular momentum up to $L = N$ and of the $1s^2$ $1S^e$ ground state is required. It has been found [26] that electron correlations have a large influence on the $1S^e$ series due to the presence of the bound $1s^2$ state, whereas for the other symmetries correlations are less important with a magnitude of 5% [26]. In the determination of multiphoton detachment rates of H^- , it is important to calculate the ground state accurately and use this state consistently in the entire detachment calculation. Otherwise, an incorrect ground state may appear as a spurious resonance in the detachment spectrum. The continuum states and the ground state therefore have to be calculated simultaneously and the basis set used to determine the $1S^e$ wave

functions differs significantly from the basis sets used for the other symmetries.

To determine low continuum wave functions as well as the highly correlated ground state simultaneously and accurately we employ a technique based on a combination of two different hydrogenic B -spline-based basis sets. The first B -spline set, which is adapted to generate accurate continuum wave functions, consists of 134 splines of order 7 with a composite knot distribution. From 0 to 40 a.u., 30 knot points are distributed exponentially to describe the behavior near the nucleus, and from 40 a.u. to the cavity radius R , 102 knot points are defined with a linear spacing to describe the oscillatory nature of the continuum wave functions in the energy range of interest. The cavity boundaries are multiple knot points and applying the conditions, that the wave functions vanish at the cavity boundaries results in a total of 134 spline solutions. Since the oscillations of the required continuum wave functions have a long wavelength, a relatively small number of B splines is sufficient to describe them accurately even for a large value of R . Solutions have been obtained for l values up to 7.

The continuum wave functions are confined within a box and are therefore normalized to unity instead of the usual δ -function normalization. The size of the cavity defines the density of states in the energy range of the detached (free) electrons, similar to the way the density of vibration frequencies of a string varies with the length of the string. When the order of the process increases the energy range of the continuum electrons becomes smaller and contains less discretized energy values. In order to ensure that there still is a reasonable number of energy values within this energy range the density of states must be increased and this is achieved by enlarging the cavity. The cavity radii used vary from 400 a.u. for two- and three-photon transitions to 800 a.u. for four- and five-photon transitions. At low continuum energies, this has the effect of doubling the number of final states within a given energy range. For higher-order processes, the oscillations of the continuum wave functions have a longer wavelength and the extended box size may still be used with the same number of B splines. It was checked that the final results do not depend on the cavity sizes used. For six-photon transitions, the cavity size is reduced to 600 a.u. and the number of splines in the linear region is increased to 132, as will be discussed later.

The second hydrogenic basis set, used to determine the electron-electron correlation effects for the H^- ground state, consists of only 20 splines of order 7 distributed exponentially from 0 to 200 a.u. Solutions with l values up to 2 have been obtained. As this basis set is mainly used for the determination of the ground state, a relatively small number of spline solutions is sufficient and a smaller size of the cavity can be used since the correlation effects are expected to be large only close to the nucleus.

These B -spline basis sets are used to solve the Schrödinger equation for the neutral one-electron hydrogen atom confined to a box. The lowest solutions obtained using the large B -spline expansion compare very well to the real hydrogenic wave functions. For the equiv-

alent solutions obtained using the smaller B -spline basis set, the agreement is only slightly less satisfactory. Products of the hydrogen wave functions obtained in this way are subsequently used to define the two-electron basis set.

For the $^1S^e$ states both sets of hydrogenic basis states are used. The basis comprises the discretized $1s$ $n/\epsilon s$, $2s$ $n/\epsilon s$, and the $2p$ $n/\epsilon p$ series built from the first set of B -spline solutions, and to these series we add all configurations s^2 , p^2 , and d^2 (including configurations with nonequivalent electrons) in which no $1s$, $2s$, or $2p$ electron is present, built from the second set. Although only discretized states are included, we use the notation n/ϵ to indicate that the effects of all bound states and all continuum states are included. This combined basis allows for an accurate description of the continuum wave functions as well as the $1s^2$ ground state. The requirement for the applicability of this approach is the orthogonality between the $1s$, $2s$, and $2p$ functions from the different basis sets. The orthogonality is worst for the $2s$ state with an error of 1×10^{-6} . From a comparison of the transition amplitudes for the $1s$ to $2p$ transition, a relative error of 10^{-6} is observed. In the calculation of the dipole transitions between $^1S^e$ and $^1P^o$ states, the nonorthogonality of the spectator electron is taken into account. For other transitions, there are no nonorthogonalities. It is assumed that this accuracy is sufficient for the present purposes.

For the other symmetries, with $L \geq 1$, the basis set consists only of the $1s$ $n/\epsilon l$, $2s$ $n/\epsilon l$, $2p$ $n/\epsilon(l-1)$, and $2p$ $n/\epsilon(l+1)$ continua with $l = L$ and single-electron wave functions obtained from the first B -spline basis set. For these symmetries no stable bound states exist and as a consequence correlation effects are smaller. The most important correlation effects are taken into account by including the $2p\epsilon l'$ continua in the calculation.

These two-electron basis sets are used in a configuration-interaction calculation with the electron-electron repulsion included. A complete diagonalization of the resulting matrix of size 972 ($^1S^e$ symmetry) or 536 (other symmetries) is carried out, since all eigenstates are required in the determination of the detachment rates. The number of continuum states that lie in the range of energies with which electrons can be detached after absorption of N photons is always kept to about 20–30 by varying the cavity size as mentioned earlier. Subsequently, the dipole interaction between all eigenstates is calculated using the continuum eigenfunctions normalized to unity. With the aid of Eqs. (1) and (2) the detachment rates are obtained. Finally, the wave functions are normalized using a central difference approximation for the energy density, given by [34,40]

$$\rho(E_K) = \frac{2}{E_{K+1} - E_{K-1}}, \quad (4)$$

in which E_K is the energy of the B -spline discretization of a continuum eigenfunction. Each series is ordered with respect to energy and K indicates the number of the wave function within the series. Using Eq. (4) the continuum functions are transformed into proper continuum wave functions obeying the δ -function normalization when they are extended to infinity. This renormaliza-

tion is not required for intermediate states. It is noted that the continuum wave functions behave like Bessel functions for large r as electron detachment results in a neutral H atom. For the normalization of the lowest discretized continuum state E_{K-1} is replaced by the hydrogenic $1s$ energy. No excess-photon detachment rates are calculated and the intermediate energies thus lie below the H^- photodetachment threshold. Therefore, no accidental degeneracies between intermediate states and discretized continuum states are possible and there are no complications involved in evaluating Eq. (2).

III. RESULTS

Here the multiphoton detachment rates for the case of linearly polarized light are presented. For a good description of the properties of H^- , electron-correlation effects have to be included. In the present approach an $1s^2$ ground state energy of -0.527432 a.u. is found, compared to the "exact" value -0.527751 a.u. due to Pekeris [41]. The agreement for the H^- ground state energy can be improved by including configurations of the type l^2 with higher angular momenta, but the increase in accuracy with l is fairly slow. The expected increase in accuracy does not compensate for the increase in CPU time and memory requirements. Since our primary interest is the determination of multiphoton detachment rates, we have not improved further on the description of the ground state. The difference in electron affinity corresponds to a shift in the photon energy of $70/N$ cm^{-1} at the threshold for N -photon absorption to $70/(N-1)$ cm^{-1} at the threshold for $(N-1)$ -photon absorption.

The detachment rates are obtained at discrete energy points, the energies of the discretized continuum wave functions. The energies do not necessarily coincide for all open channels, but the smoothness and density of the data points are high enough to allow the use of cubic-spline interpolation to obtain the detachment rates at intermediate energies. The summation over all partial detachment rates is straightforward. In the figures shown here, we show the interpolated curves from the threshold for N -photon absorption to the threshold for $(N-1)$ -photon absorption. For two- to four-photon detachment, the results are compared to other theoretical calculations [26,27,29,30], which include electron correlation. Finally, the results are compared to detachment rates obtained using model potential methods [24].

In Fig. 1 the two-photon detachment rate of H^- as a function of photon energy is shown as well as the partial contributions from the two available final symmetries, $^1S^e$ and $^1D^e$, using the present approach. The total detachment rate shows the usual Wigner-law behavior for $^1S^e$ final states with a fast increase, which soon reaches a maximum value of $4.5 \times 10^5 I^2$ a.u. at a photon energy of 3300 cm^{-1} with the $^1S^e$ channel reaching a maximum intensity of 4.2×10^5 a.u. at a photon energy of 3150 cm^{-1} . For higher energies only a slow decrease in the total detachment rate is observed since the $^1D^e$ channel, which is populated to a lesser extent for low photon energies because of the rotational barrier making it difficult for low

FIG. 1. Partial and total two-photon detachment rates divided by I^2 for H^- as a function of photon energy. The total detachment rate is indicated by the solid line, whereas detachment into the $^1S^e$ channel is indicated by the dashed line and detachment towards $^1D^e$ final states by the dotted line.

continuum d electrons to penetrate the interaction region, increases in importance quickly. Around 3800 cm^{-1} the dominant detachment channel changes from $^1S^e$ to $^1D^e$. From the behavior of the partial waves it can be seen that a dramatic change in the angular distribution may be observed with an isotropic distribution around 3100 cm^{-1} due to the dominance of the $^1S^e$ channel, whereas the distribution is expected to become anisotropic for photon energies in the order of 5500 cm^{-1} .

In Fig. 2 total detachment rates obtained by different theoretical approaches are shown. The B -spline result for the total detachment rate compares well with the results obtained by Proulx and Shakeshaft [29] and by Liu *et al.* [30] with a relative disagreement of at most 10%, which is the same disagreement as between Proulx and Shakeshaft [29] and Liu *et al.* [30]. For photon energies higher than 3800 cm^{-1} , the agreement between our calculation

FIG. 2. Comparison of total two-photon detachment rates divided by I^2 for H^- obtained by the present approach (solid line), Proulx and Shakeshaft [29] (long dashes), Liu *et al.* [30] (dotted line), Crance [26] (short dashes), and Mercouris and Nicolaides [27] (crosses).

and Proulx and Shakeshaft [29] is well within 5%. The most prominent disagreement is the location of the maximum, which is shifted towards lower photon energy in the present calculation. The increase in detachment rate for low photon energies is more rapid than for the results due to Proulx and Shakeshaft. However, they noted that their results were less accurate in this region. At 3700 cm^{-1} a significant disagreement with Proulx and Shakeshaft is found in the functional behavior, at which photon energy they report a small dip in the detachment rate, for which no evidence is found in the present calculations. It is noted that they obtained a better electron affinity since they included f^2 configurations in the $1S^e$ calculation. The relative difference with Liu *et al.* is more or less constant up to a photon energy of 5000 cm^{-1} and decreases for higher photon energies. Aside from the difference in the position of maximum detachment rate, there is very good agreement in the functional behavior between the present calculation and the one by Liu *et al.*

The agreement with the calculations by Crance [26] is worse with a difference of about a factor of 2. The electron affinity obtained by Crance, 0.02733 a.u. , is slightly smaller than obtained here. The basis set used in Ref. [26] consisted of 60 Slater functions for each angular symmetry and possibly this expansion is too small. The results due to Mercouris and Nicolaides [27] agree quite well in magnitude for larger photon energies, but for smaller photon energies they obtain much larger detachment rates. They obtained detachment rates at a rather limited number of energies and it is therefore difficult to make a detailed comparison for low photon energies. For high photon energies good agreement is found.

Finally, our results are compared with results obtained using the various model potential methods due to Geltman [24]. Geltman reported total and partial detachment cross sections for two- and three-photon processes in several model potentials, but here we will only consider results obtained using a δ -function potential (DFP) and in particular a short-range model potential combined with continuum wave functions employing the experimental phase shift (MPPS) since this potential gives best agreement. It is noted that in this approach the continuum wave functions have a discontinuous first derivative and that, as mentioned, experimental results are required to construct the potential.

Using the DFP [24], the total detachment spectra show additional structure with a minimum detachment rate at a photon energy of 4700 cm^{-1} , a feature not observed in other calculations. Near the threshold for two-photon absorption, the DFP partial detachment spectra differ considerably from the present calculations. The difference in the total detachment rate between the MPPS and the present results is much better, of the order of 10%. For the partial widths, the agreement with the present results for detachment into $1S^e$ and $1D^e$ detachment channels is reasonably good, although the shape of the partial detachment rates differs considerably near the threshold for one-photon absorption. At these energies, a sudden increase in the $1S^e$ detachment rate is observed, which is not present in the B -spline results. The MPPS is nevertheless well suited for theoretical investigations

for multiphoton detachment in the lower energy region.

In Fig. 3 the partial and total rates for three-photon detachment divided by I^3 are shown. The final states can have either $1P^o$ or $1F^o$ symmetry. The total three-photon detachment rate rises quickly, but, in agreement with the Wigner law, slower than that observed for $1S^e$ in the two-photon detachment results, to a maximum of $5.2 \times 10^{10} I^3 \text{ a.u.}$ around 2200 cm^{-1} followed by a much sharper decrease than that observed for two-photon detachment. The maxima for detachment into $1P^o$ and for the total detachment rate coincide for three-photon detachment. The explanation for the sharp decrease is that the three-photon process hardly populates the $1F^o$ continuum and only when the photon energy exceeds 2700 cm^{-1} the detachment is mainly into the $1F^o$ continuum. The angular distributions in three-photon detachment will show less change since the decay is dominated by the $1P^o$ channel. Only for the high region, $1F^o$ final states dominate, but here the detachment rates are smaller and in the determination of angular distributions a large cross section is required since only a fraction of the total electron emission is monitored.

There are two reasons why the $1P^o$ continuum is dominant in three-photon absorption in H^- . The first reason is that only a $1S^e$ bound state exists. Upon examination of the virtual intermediate states, it is found that a large contribution to the virtual intermediate $1S^e$ state (reached after absorption of two photons) is a ground state admixture, which gives rise to a large dipole matrix element. Since there is no counterpart in the $1D^e$ manifold, the ground state component significantly increases multiphoton detachment rates in the $1P^o$ channel relative to the other channel. The second reason is that in this system low energy continuum functions with high angular momenta have a small amplitude in the neighborhood of the nucleus due to the rotational barrier. Since tran-

FIG. 3. Partial and total three-photon detachment rates divided by I^3 for H^- as a function of photon energy. The total detachment rate is indicated by the solid line, whereas detachment into the $1P^o$ channel is indicated by the dashed line and detachment towards $1F^o$ final states by the dotted line.

sitions take place only in the presence of an electrostatic potential and the H^- binding potential falls off rapidly with r , the transition probabilities for high l values decrease as well.

In Fig. 4 the total detachment rates obtained from various approaches are compared. A comparison with the results due to Proulx and Shakeshaft [29] shows good agreement. They obtain a maximum detachment rate of $4.8 \times 10^{10} I^3$ a.u. at a photon energy around 2200 cm^{-1} , which is slightly larger than the energy for maximum detachment found in the present calculation. At larger photon energies, very good agreement is observed. The agreement with Liu *et al.* [30] is also good, with a difference for high photon energies of 10%, while it is smaller for low photon energies. Their maximum detachment rate is $5.4 \times 10^{10} I^3$ a.u. at the same photon energy as that calculated by Proulx and Shakeshaft [29], a difference of over 10% between these two calculations. For lower energies, our results confirm the results of Liu *et al.* [30], whereas at higher energies our results are in better agreement with the spectrum obtained by Proulx and Shakeshaft [29].

The results obtained by Crance [26] are about a factor of 3 smaller than the results from the B -spline calculation. However, the overall behavior of the detachment rates is in good agreement, although the frequencies at which maximum detachment is observed differ by about 75 cm^{-1} . A comparison with Mercouris and Nicolaides [27] shows that the rates are in good agreement with regard to magnitude. However, their spectrum appears to be shifted in photon energy by more than 100 cm^{-1} .

The difference in detachment rate between the present spectrum and the one determined by Geltman [24] using the MPPS potential is about 15%. The agreement in the overall behavior of the detachment rates is very good, also in the energy range close to two-photon detachment. When comparing the partial detachment rates for three-photon detachment, the dominance of the $^1P^o$

FIG. 4. Comparison of total three-photon detachment rates divided by I^3 for H^- obtained by the present approach (solid line), Proulx and Shakeshaft [29] (long dashes), Liu *et al.* [30] (dotted), Crance [26] (short dashes), and Mercouris and Nicolaides [27] (crosses).

final channel is clear. The partial detachment spectra obtained here and in the MPPS calculations agree very well, except near the threshold for two-photon absorption.

Geltman [24] obtained a three-photon absorption spectrum using the DFP as well. The agreement between our spectrum and the DFP is better than with the MPPS spectra for frequencies lower than 2300 cm^{-1} , but for higher frequencies differences up to 25% are observed (see also [30]). The good agreement for three-photon absorption and the poorer agreement for two-photon absorption rates between the different methods indicate that the three-photon absorption spectrum is less suited for examining the accuracy of various model potentials.

An experimental three-photon detachment spectrum has been obtained by Smith *et al.* [16]. It is difficult to make a comparison with their results due to the large signal-to-noise ratio in their spectra and due to the absence of structure in both the experimental and the theoretical spectra. The accuracy of the experiments performed in the four-photon detachment range [14] is worse. As noted in [16], "It does not make sense to try to fit the preliminary data of ... [14] quantitatively to theory."

The four-photon detachment rates divided by I^4 are shown in Fig. 5. The three final symmetries are $^1S^e$, $^1D^e$, and $^1G^e$. The behavior of the total detachment rate is different from the behavior found for two-photon and three-photon detachment. At a photon energy of 1550 cm^{-1} a maximum of $6.8 \times 10^{15} I^4$ a.u. is found. At higher photon energies a shoulder is observed, followed by a slow decrease of the detachment rate. The reason for this behavior is easily understood by a breakdown into the different partial rates. Detachment into $^1S^e$ states has a slightly larger magnitude than detachment into $^1D^e$ and since the $^1D^e$ states are populated at

FIG. 5. Partial and total four-photon detachment rates divided by I^4 for H^- as a function of photon energy. The total detachment rate is indicated by the solid line, whereas detachment into the $^1S^e$ channel is indicated by the dashed line and detachment towards $^1D^e$ final states by the dotted line. Detachment into the $^1G^e$ continuum is indicated by the dash-dotted line.

higher photon energies than the $1S^e$ states, this results in a shoulder in the total detachment spectrum. The $1G^e$ final states have a fairly small contribution, which becomes non-negligible only for higher frequencies. However, for the $1S^e$ spectrum, it is observed that the rate reaches a minimum with a negligible detachment rate at a frequency of about 1790 cm^{-1} . This behavior is due to the transition probability from the highest virtual intermediate state to the final continuum state and does not originate from interference between the two possible paths to the final $1S^e$ continuum. At this frequency there is no isotropic component expected in the angular distributions.

The only previous calculations of four-photon detachment rates with a full inclusion of electron correlation have been performed by Crance [26] and by Mercouris and Nicolaides [28]. However, for two-photon and three-photon detachment, it has been found that the agreement with the calculations by Crance was rather poor and it cannot be expected that the agreement will improve when going to higher-order processes. This is in fact the case and we do not compare with her results for four- and five-photon detachment.

The present results and the results obtained by Mercouris and Nicolaides [28] show a reasonably similar behavior of the detachment rate with respect to the photon energy. In their calculation, the shoulder structure due to the $1D^e$ continuum is much more prominent and appears as an additional peak. Also the relative intensities of the peak and the shoulder are different. For the total intensity, there appears to be a reasonable agreement with a difference of about 30%, although it is difficult to obtain an accurate value for the total detachment cross section from their figure due to the logarithmic scale they use.

The four-photon spectra show much more structure than the two-photon spectra and there is a large influence from the $1S^e$ channel, which is (virtually) present after absorption of two photons and is difficult to describe in a model potential approach. In view of the importance of this intermediate state, it is expected that the differences between model potential approaches and descriptions with electron correlation included will be more pronounced in the four-photon detachment spectrum than for lower order detachment. DFP and MPPS results for four-photon absorption would therefore be very interesting.

In Fig. 6 the five-photon detachment rates divided by I^5 are shown. The final symmetries include $1P^o$, $1F^o$, and $1H^o$. There is little structure in the total detachment rates with a maximum around 1260 cm^{-1} followed by a slow decrease, which reflects the dominance of the detachment into the $1P^o$ channel. It is remarkable that the increase in detachment rate is much larger going from four-photon detachment to five-photon detachment than going from two- to three-photon detachment or from three- to four-photon detachment. Near the threshold for four-photon detachment, a slight increase in detachment rate is found and a minimum is found at a frequency of 1420 cm^{-1} . Compared to the three-photon detachment rates, the $1F^o$ channel has gained considerably in impor-

FIG. 6. Partial and total five-photon detachment rates divided by I^5 for H^- as a function of photon energy. The total detachment rate is indicated by the solid line, whereas detachment into the $1P^o$ channel is indicated by the dashed line and detachment towards $1F^o$ final states by the dotted line. Detachment into the $1H^o$ continuum is indicated by the dash-dotted line.

tance, although the spectrum is still dominated by $1P^o$ final states. On the other hand, at a photon energy of 1420 cm^{-1} the contribution from $1P^o$ has vanished. The $1H^o$ contribution is negligible over the entire frequency range.

In Fig. 7 we present results of the calculation of six-photon detachment rates with correlation fully included. The total rate divided by I^6 as well as partial rates toward $1S^e$, $1D^e$, and $1G^e$ final states are given. The $1I^e$ states can also be reached with six-photon transitions,

FIG. 7. Partial and total two-photon detachment rates divided by I^6 for H^- as a function of photon energy. The total detachment rate is indicated by the solid line, whereas detachment into the $1S^e$ channel is indicated by the dashed line and detachment towards $1D^e$ final states by the dotted line. Detachment into the $1G^e$ continuum is indicated by the dash-dotted line, while detachment towards $1I^e$ final states is completely negligible for linearly polarized light and therefore not shown.

but the intensity of these transitions is negligible using linearly polarized light, although for circularly polarized light, these are the only final states that can be populated. In the calculation of these detachment rates, a significant influence from doubly excited states on the detachment rates can be expected. These high-lying states can be excited from the $1s^2\ ^1S^e$ components and can also deexcite to this component. Since in the intermediate $^1S^e$ states the $1s^2$ component is important, these excitation paths may become more important when the order of the process increases. For higher-order processes, it becomes possible to have transitions between doubly excited states and transitions between doubly excited states and continuum functions in the energy range of the doubly excited states. The presence of these transitions means that not only low-energy continuum functions must be represented accurately, but also the continuum functions in the energy range of the doubly excited states. This was achieved by reducing the box size to 600 a.u. combined with enlarging the number of B splines in the linear region to 130, giving a total number of 162 B -spline solutions. The most interesting feature is that the maximum detachment rate is no longer observed in the lowest frequency range, but has shifted towards the middle of the six-photon detachment range, 1075 cm^{-1} , with a shoulder at lower frequency. From a breakdown into the different angular components, it can be seen that the second maximum is due to the $^1D^e$ continuum giving rise to the largest detachment rates, the continuation of a feature already present in the four-photon detachment spectrum.

IV. CONCLUSIONS

A method based on the use of B splines has been developed to generate total as well as partial N -photon transitions detachment rates for H^- in a perturbative approach with N up to 6. It is demonstrated that the use of two B -spline sets gives accurate solutions including electron correlations for both bound state as well as continuum wave functions in the case of a two-electron negative ion. Reliable transition probabilities for radiative transitions have been obtained. The results for two- and three-photon detachment obtained by this method compare well with other perturbative approaches using Sturmian and hyperspherical basis sets, although best agreement with Sturmians is found at low photon energies and with hyperspherical functions at high photon energies.

Higher angular-momenta gain importance in higher-order interactions between negative ions and light. In neutral atoms, intermediate resonance effects have dramatic influences on the distribution of electrons over the final detachment channels, but the negative hydrogen ion offers the possibility to investigate multiphoton processes without additional resonance structures. Little structure is observed in the total detachment rates versus frequency. For four-photon and six-photon detachment $^1D^e$ is the main detachment channel, while for absorption of fewer photons, the channel with lowest L is dominant. In the partial widths, structure is much more pronounced with minima in the detachment for the $^1S^e$ states starting with four-photon transitions, and for the $^1P^o$ states starting with five-photon transitions.

The most recent calculations including correlation between the electrons are in good agreement with each other. However, for more complex negative ions approximations have to be made and it is therefore interesting to see whether the behavior of negative ions in light fields can be described by generalizations of the H^- results. Since in lowest nonvanishing order of perturbation theory the correlation effects are described accurately, it is possible to judge the many model potential calculations for H^- on their merits. A δ -function potential gives a too simple description of H^- , but using much more sophisticated model potentials such as the MPPS, a good description of the negative hydrogen ion can be obtained. However, to develop such model potentials experimental results are necessary, but if such data are available, the success of the MPPS for H^- indicates that this model perhaps can give reliable results at least for two- and three-photon absorption. Detachment spectra for four-photon absorption would be very suitable for a closer examination of the accuracy of model potential approaches since in four-photon detachment two non-negligible final channels are available and the ground state has a significant contribution via an intermediate state.

ACKNOWLEDGMENTS

The author would like to thank Dr. H. Rudolph for his interest in this work and for numerous fruitful discussions, Dr. J. E. Hansen for carefully reading the manuscript, and Professor H. B. van Linden van den Heuvell and Dr. M. D. Davidson for their interest in this work.

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