Two-Electron Photoejection of He and H^-

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In order to overcome difficulties in the description of the two-electron continuum problem, we develop a finite element method to treat two-electron escape processes. Two-electron photoejection cross sections are obtained for helium and H^- at photon energies in the range of 79–460 and 14.4–110 eV. The H^- double detachment calculations are apparently the first nonperturbative quantum results in this energy range since the pioneering work of Broad and Reinhardt in 1976. Our branching ratio between single and double detachment of H^- peaks at a value 25%–40% higher than the results from that early study. [S0031-9007(97)03475-3]

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An accurate quantitative description of two-electron escape processes in the low and intermediate energy regions has eluded theoretical attempts for decades. At very high energies, perturbative approaches such as many-body perturbation theory, the Born approximation, or distorted-wave Born-type approximations are capable of describing these processes adequately. The accuracy of perturbative approaches deteriorates rapidly as the photon energy decreases to within a factor of 2 to 3 times the double escape threshold energy. In this energy region, electron-electron correlations must be treated nonperturbatively. At energies just above threshold, such correlations are important out to very large distances from the target. The present Letter focuses on the intermediate energy range, where electron-electron correlation effects require a nonperturbative treatment, yet are confined sufficiently close to the target to permit an accurate numerical description.

Helium double photoionization processes have received a tremendous amount of attention from both theory [1–6] and experiment [7–10]. The ratio of double to single photoionization serves as a good measure of the electron interaction strength, because it would vanish to zeroth order in $1/r_{12}$. Remarkably, however, there has been much disagreement about the maximum value of the ratio, from both experiment and theory. The maximum value of this ratio occurs for photon energies in the range of 150–250 eV. It has been predicted and measured to reach values that peak anywhere from 0.030 to 0.055 before the ratio falls slowly to an asymptotic value of 0.0167 at high energies [11–14]. The discrepancies among different results for this branching ratio exemplify the difficulties that have been encountered by theoretical attempts to describe the comparatively infrequent two-electron escape processes in this energy range.

Studies of one- and two-electron photoejection from H^- at photon energies above the double escape threshold have been far more limited than those for helium. The determination of H^- photodetachment cross sections has received a considerable amount of attention for low photon energies [15], in part due to its importance in astrophysics. The threshold law for double photodetachment of H^- has been explored both theoretically [16] and experimentally [17], but the applicability of these studies is restricted to just the first 1 or 2 eV above threshold. To the best of our knowledge, no experimental results exist, and only a single theoretical study has been performed to address photoejection of H^- at higher energies. This study was performed by Broad and Reinhardt over twenty years ago using a multichannel J-matrix technique with an L^2 basis set [18]. Total photodetachment cross sections were presented for photon energies in the range of 1–69 eV. They stated that their two-electron photoejection cross sections were converged to within 15% and in the manuscript quoted a value for this ratio that was approximately 0.04 over this energy range. Examination of their data suggest that the ratio σ_{2e}/σ_{1e} obtained in those calculations reached a maximum value in the range of 0.055–0.085. Fluctuations in the reported results, of the type often seen for an L^2 representation of the two-electron continuum, can probably be viewed as providing an approximate "error bar" ± 0.020 on the results of Broad and Reinhardt.

Like helium, H^- is an ideal prototype system for the study of two-electron photoejection, because of its inherent simplicity. Important differences exist, however, between double photoionization of helium and double photodetachment of H^-. First, the ratio between the single and double escape threshold energies is much smaller for H^- than for He, as H^- has just one bound state. Secondly, while a single electron escape process of helium occurs with the "outer" electron in a screened Coulomb potential (to first approximation), single electron escape of H^- leaves behind a neutral atom. Because of the smaller nuclear charge, one expects electron interaction effects to exert an even greater control over the dynamics of photoejection in H^-.

The greatest obstacle to the theoretical description of two-electron escape derives from an inadequate understanding of how to impose the proper boundary conditions at infinity. We avoid this difficulty by imposing boundary

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conditions at the surface of a finite volume rather than at infinity. In this investigation, we utilize the eigenchannel *R*-matrix method to calculate approximate wave functions that can be used to calculate the probability of two-electron escape. The underlying idea of *R*-matrix theory is to separate configuration space into an "inner" region (called the reaction volume or "box") and an "outer" region. In the inner region, where both electrons are near the nucleus, we treat the problem "almost exactly" by including all electron-electron correlation effects. In the outer region, where one electron is far removed from the nucleus, we make the approximation that the inner electron completely shields the nucleus, so that the outer electron experiences only a Coulombic potential from a constant screened charge $Z - 1$, with Z the nuclear charge. This approximation is sensible for the final state only if there is unequal energy sharing among the two electrons. That is, for the case of double photoejection, if one electron receives most of the photon's energy and quickly leaves the atom. The remaining electron is left near the nucleus temporarily before eventually escaping. Double escape events at energies just above threshold are known [19–21] to occur with nearly equal probabilities for all possible values of E_2/E_1; therefore, our approximation scheme is poorest at low energies. Already at a few eV above threshold, however, double escape is dominated by unequal energy sharing processes, as has been shown by experiment [22]. In part for this reason, in part because of the stability and robustness of the present calculations, and in part because of the agreement among our calculations performed using different gauge forms, we are confident that the results presented in this Letter are valid at all photon energies shown, except within a few eV of threshold.

The eigenchannel *R*-matrix method has successfully described multichannel single electron escape [23] for a number of atoms. In an earlier application of this method to helium double photoionization, we found cross sections that were slightly lower than the experimental data [5] available at that time. Experiments performed since then [8–10] have been in closer agreement with our first calculated cross sections performed with the basic "scheme" presented there than with the experiments and theory. A subsequent application of the eigenchannel *R*-matrix approach to a simplified model of electron-hydrogen (and electron-He^+) scattering [24] indicated that this method could describe two-electron escape processes accurately. The initial application to helium double photoionization was disappointing in one aspect: A discrepancy between the various forms used in calculating dipole matrix elements indicated inaccuracies in the initial and/or final state wave functions. The discrepancy between the velocity and acceleration forms was significant, and the length form gave results that were much higher (and obviously unphysically so) than those of either the velocity or acceleration form. (Unreasonable results for the length form have also been reported in an application of the convergent close-coupling method to this problem by Kheifets and Bray [6].)

The key difference between the current approach and our previous application involves our choice for the variational basis set. Instead of forming a two electron *global* basis set consisting of products of one-electron hydrogenic orbitals, a *local* finite element basis set is adopted for the present study. Our expectation was that the finite element method (or other local basis set methods, e.g., *B*-splines) should be able to represent the initial and final wave functions more accurately, which should in turn reduce the discrepancy among the different forms. The suitability of a finite element approach for calculating accurate bound state wave functions has been previously illustrated [25]. It was also adapted to the calculation of accurate bound state excitation cross sections in electron-hydrogen scattering by Shertzer and Botero [26]. In this Letter we report the first application of a finite element basis set to *two-electron escape processes*.

We calculate the ratio of double to single photoejection cross sections of helium and H^- for photon energies of 79–460 and 14.35–110 eV. Approximately 180 h of supercomputer time on a SGI Power Challenge machine was used to calculate these cross sections. The results presented here were obtained by using three partial waves in the initial state and four partial waves in the final state. Box averaging was used to obtain the cross section profiles presented here, and a frame transformation was used in order to separate out the single and double photoejection contributions (see [24] for details of these techniques). A Gailitis averaging technique can be used to eliminate Rydberg series of pseudoresonances in the double continuum [24]. This averaging scheme was adopted in obtaining results for helium, but was inapplicable to our H^- calculations, as no long range Coulomb field is present in this process. Our calculated ground state energy of helium of –2.9028 a.u. agrees well with the "exact" (infinite mass) value of –2.9037 a.u., as does our ground state energy of H^- of –0.52744 with the exact value of –0.52775 a.u. (exact nonrelativistic infinite mass values are taken from Ref. [27]).

Our results for the ratio of double to single photoionization for helium are compared to recent theoretical and experimental values in Fig. 1. Experimental measurements of this ratio by Dörner *et al.* [9] and Levin *et al.* [8] over the intermediate energy range are similar in profile, but differ in magnitude by 10%–20%. Samson's values [10] in Fig. 1 have actually been "smoothed," but the smoothed values differ very little from the original experimental values (on the order of a couple of percent). The error bar associated with Samson's measurements is roughly 5%, while Levin's experimental error bar is comparable to the scatter in his reported values, as seen in Fig. 1. Recent theoretical calculations of the ratio include the convergent close-coupling calculations of

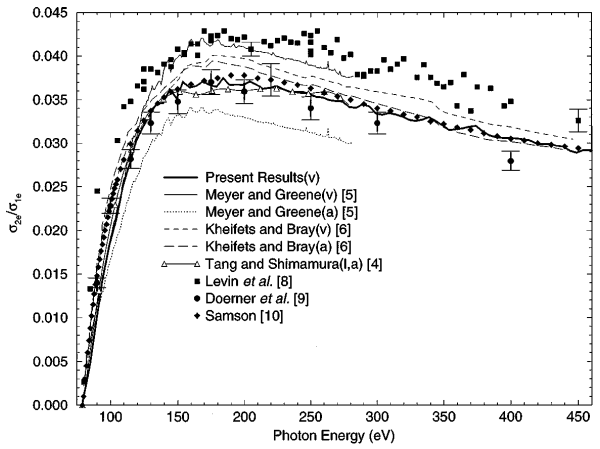

FIG. 1. Comparison of the ratio of double to single photoionization for helium with other theoretical and experimental values. Our results in a previous study are shown by the narrow solid and dotted lines.

Kheifets and Bray [6], the hyperspherical close-coupling calculations of Tang and Shimamura [4], and our previous eigenchannel *R*-matrix calculations using a hydrogenic basis set [5]. Our finite element results for photon energies of 80–280 eV were obtained by box averaging over five box sizes in the range 12–16 a.u., while the results for 280–460 eV were obtained with a single box size of 10 a.u. A smaller reaction volume can be used at higher energies since electron correlation effects are more tightly confined near the nucleus. Our calculated values of the ratio are below most of the other theoretical and experimental values for the first few eV above threshold, the region where our approximation of unequal energy sharing is expected to break down. At higher energies our calculated results agree accurately with the experimental values of Samson and co-workers. Our results are also consistent with those of Dörner *et al.* [9] except for his highest energy measurement.

Figure 1 shows only our velocity form calculations. Calculations performed using the acceleration form of the dipole operator are nearly identical (agreement to better than 1%) to those of the velocity form over the entire energy range shown. This is in contrast to the results of our previous study (shown by the narrow solid and dotted lines in Fig. 1) using a hydrogenic basis set in which the discrepancy between the velocity and acceleration forms was 20%–25%. Furthermore, the length form results from our previous study gave double ionization cross sections an order of magnitude larger than in the other forms. In the present study, calculations in the length form are found to agree closely with the other forms up to about 100 eV above the double escape threshold before slowly diverging. At the highest energies shown in Fig. 1, length form calculations give a double ionization cross section which is about 10%–15% higher than the other forms. Although the use of a finite element basis set requires a much greater computational effort than the use of a hydrogenic basis set, this choice of basis set can be systematically improved with less effort. The resulting improved agreement among the length, velocity, and acceleration forms is dramatic, which shows the power of finite element techniques for such problems.

Our results for the double to single photoejection ratio in H^- are shown in Fig. 2. We averaged our calculation over five box radii in the range 24–32 a.u. for photon energies of 14.35–65 eV, and over two box radii of 24 and 26 a.u. for photon energies of 65–95 eV. The results for 95–110 eV were obtained with a single box radius of 24 a.u. A box of roughly twice the radius used in our helium calculations is required to accurately describe H^- photodetachment, since hydrogen wave functions extend roughly twice as far as those of He^+. The smoothed curve of our data was obtained by convolving our box averaged values (open circles) with a Gaussian function. The three graphs of Broad and Reinhardt [18] in Fig. 2 were obtained by using different choices of final state basis sets. Our values for the H^- total photoabsorption cross section agree well with those of Broad and Reinhardt, as do our values for the $n = 1$ and $n = 2$ partial cross sections. However, our peak branching ratio for double photodetachment is significantly larger than their values. The maximum value of our ratio of 0.094 ± 0.006 lies in the photon energy range of 25–35 eV. We believe that our new calculations are more accurate than the results of Broad and Reinhardt; this is suggested by the smaller amount of scatter among our results in Fig. 1. On the other hand, our results are not in serious disagreement with their calculations, when their relatively large "theoretical error bars" are taken into account. In that sense the two calculations appear to be consistent,

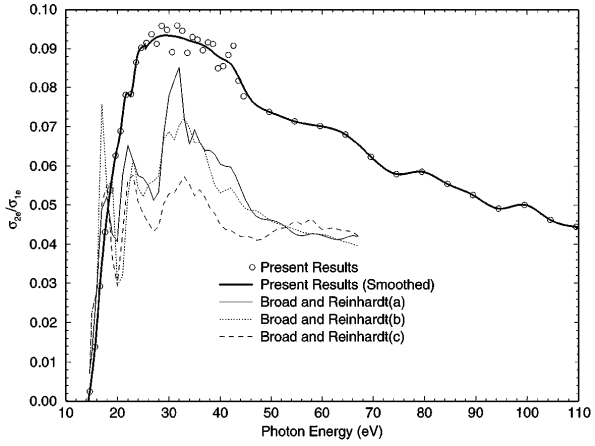

FIG. 2. Comparison of the ratio of double to single photodetachment for H^- with previous calculations of Broad and Reinhardt [18]. The results of Broad and Reinhardt were obtained using the final state basis sets: (a) $10s, 10p, 6d$, (b) $7s, 10p, 6d$, and (c) $7s, 10p, 6d, 4f$.

and the ground breaking work of Ref. [18] is impressive in view of the computational resources then available.

It is informative to contrast the nature of two-electron escape processes in helium and H^-. To a first approximation, one might expect the maximum in the ratio of double to single photoejection to scale as a simple function of the charge of the nucleus [28] (preliminary calculations of the ratio for Li^+ indicate a maximum value of roughly 0.020). However, H^- is quite different from other heliumlike systems, and should not be expected to obey any simple scaling law. In spite of this, we do observe that the peak in our double photoejection cross sections for H^-, He, and Li^+ targets occurs at roughly the same energy relative to the double escape threshold when it is scaled by $1/Z^2$. Our calculations indicate that the maximum value of the ratio for H^- of 0.094 ± 0.006 is about three times as large as the value for helium of 0.037 ± 0.001. Furthermore, the peak occurs at an energy approximately six times smaller for H^- than for helium, relative to the double escape threshold. This is consistent with the small electron affinity of H^-. Since a smaller energy is required to remove one electron in H^-, more energy is available to remove the remaining electron. The maximum value of the double photoejection cross section for H^- is found to be about $20\times$ larger than that for helium, another consequence of helium's deeper Coulombic well.

It is interesting to note that the predicted high energy limit of the branching ratio between double and single photoejection is 0.0150 for H^-, 0.0167 for He, and 0.0087 for Li^+ [11,12], while our calculations show a much larger value for the *peak* ratio for H^- than for helium. The asymptotic values for the ratio in H^- and helium might seem to contradict the idea that electron-electron correlations play a stronger role for smaller Z. One possible explanation for this discrepancy is the observation that the $n = 2$ partial cross section for H^- is comparable to the $n = 1$ cross section [18], contributing more to the single detachment cross section, and therefore less to the double detachment cross section [29].

The present results demonstrate the clear value of finite element methods for a description of double photoejection processes. The good agreement achieved between various forms of the dipole operator adds to our confidence that we have accurately described both the initial and final states. Although we have presented only *total* photoejection cross sections here, we believe it is now possible for this method to give more detailed information about the two-electron final state reached in photoabsorption, including the photoelectron distributions in energy and angle, in the intermediate energy range. Furthermore, our use of a frame transformation permits the calculation of partial cross sections for the production of excited hydrogenic bound states; this will provide another informative test of the electron interaction dynamics. It is hoped that the results presented here will stimulate further investigation of H^- photodetachment at high energies, both experimentally and theoretically.

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