ELECTRON ENERGY SPECTRA OF H⁻ AUTODETACHING STATES RESULTING FROM COLLISIONS OF H⁻ WITH He AT 1 keV

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Electron energy spectra for H⁻ autodeaching states resulting from collisions of H⁻ with He at 1 keV are rigorously calculated by including couplings between doubly excited states and continuum states and their interference with direct detachment processes. An energy sampling procedure, based on the Gauss quadratures, is used to discretize continuum states. The present theoretical result, for the first time, clarifies mechanisms of excitation to doubly excited states, quantitatively reproduces the experimental spectra first observed by Risley and Geballe in 1974, separates the contributions from each of three autodeaching states, and identifies the cause of the interference between autodeaching and direct-detaching excitation channels.

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Nearly 20 years ago, Risley and his colleagues (1-4) experimentally studied doubly excited autodetaching states of H^- in collisions with He and other gaseous targets in the energy region from 100 eV to 10 keV by examining autodetached electron energy spectra. Studies of this type in these systems are important in providing a basic theoretical physical foundation for a fundamental understanding of the $[H + 1e]$ three-body system with and without the influence of a fourth body (He) and as a chemical probe for material analysis in surface and condensed-matter physics in applied sciences. A careful analysis of these spectra would be expected to uncover much information that would deepen our understanding of atomic and molecular structures and collision dynamics. Unfortunately, however, no rigorous follow up study has been made from either the theoretical or experimental side, except for some studies to determine the detachment cross section (5-7) and resonance levels (8-9) and this result of Risley remains unexplained. The lack of activity in this area stems from theoretical difficulties in (a) treating continuum states explicitly, (b) treating negative-ion states reasonably well, and, as a result, (c) obtaining electron spectra correctly. This system is unique in the following ways:

- a) H^- is the simplest two-electron system in which electronic structure have been extensively studied quantum mechanically and in which electron correlation is known to be essential for two-electron binding (8-9).
- b) Since no singly excited state is known to exist, the energy diagram of H^- is rather simple, with the only ground H^- state and doubly excited states.
- c) The He atom has larger first-excitation and ionization energies (20 eV and 24 eV, respectively) than does H^- ; hence, can safely be treated as an "inert" object in this energy region.
- d) No important charge transfer process exists in this collision energy domain; hence, channels needing to be included in collision dynamics are rather simple.

Because of these features, this collision system provides an excellent opportunity to study

:

- (a) An electron correlation effect coupled with a dynamical process, to examine its potential role in the overall collisions dynamics;
- (b) The contrast in the ejected-electron spectrum between short-range and long-range forces due to neutral- and charged-particle impacts, respectively; and
- (c) The interference-patterns between direct detachment and autodetachment (the so-called Fano profile), for possible application in chemical analysis.

Recently, we carried out a theoretical study of the ejected-electron spectrum (EES) for doubly excited H^- resulting from collisions with $\bar{p}$ and p at 1.5 MeV (10). This study was an extension of our previous systematic study of doubly excited He^{**} atoms resulting from collisions of p , $\bar{p}$, and multiply charged ions with He atoms at 1.5 MeV (11-12). In these studies, an one-center atomic-orbital expansion method was employed with a hyperspherical coordinate approach for obtaining atomic orbitals. The shape of the EES for doubly excited H^- for a 1.5-MeV p impact was found to be very weakly influenced by long-range Coulomb distortion by the projectile and to become very similar to the line profile resulting from photodetachment of H^- (10). However, as the collision energy decreases from MeV to keV, the line profile is expected to undergo increasingly significant distortion because of the presence of the projectile; this may be called a molecular effect. Although these studies on doubly excited states of H^- and He in high-energy collisions shed much light on the dynamical role of electron correlation and interferences, the present $[H^- + He]$ system is better suited for the study of short-range interactions and electron correlation at lower energies.

In this note, we report the first rigorous calculation of the electron energy spectra for H^- autodetaching states resulting from collisions of H^- with He, identify important excitation mechanisms, make the first prediction of the identities of interferences between the direct-

detachment and autodetachment channels, and the contributions of $H^-(2p^2:1\bar{D})$ and $H^-(2s2p:1P)$ states to the spectra. Our theoretical procedures are summarized here; they have been reported previously(13). We adopted the Feshbach projection operator method, in which the Q operator covers the space spanned by both the discrete as well as autodetaching states. Since the Q space can be spanned by L^2 functions, the conventional valence-bond configuration-interaction (CI) method can be used to obtain molecular electronic states in the Q space. The stabilization procedure was adopted to ensure that the desired doubly excited states would be obtained (14). Slater-type orbitals, employed as a basis set, were taken from Ref.(15), augmented by additional 2s, 2p, 3s, 3p, and 3d orbitals for a better description of doubly excited states. Two electrons on the H atom were explicitly treated, while electrons on the He atom were approximated by a Gaussian-type pseudopotential (16). This approximation should be reasonable, at least in the present collision energy range, because (a) He electrons have large excitation energies, in contrast to those in the H^- ion, and (b) The electron-He interaction has a uniformly repulsive nature (17). The asymptotic energy levels we obtained are within 0.2%, 0.6%, 2.3% and 4.2% of the best available theoretical results (8) for the ground $H^-(1s^2)$, $H^-(2s^2)$, $H^-(2p^2)$ and $H^-(2s2p)$, levels, respectively. These are considered to be an acceptable accuracies for the present purpose. Energy levels for our $[H(1s) + He]$ and $[H(n=2) + He]$ levels match exactly.

Continuum states were obtained by the exact static-exchange approximation to elastic electron scattering from HHe molecules (17). The continuum states were properly discretized by using energy samplings based on the Gaussian quadrature. All of continuum states were selected around resonance levels with an energy mesh size less than 0.001 a.u., sufficient to cover the effective range of each coupling between a doubly excited state and the continuum states. The continuum states in nonresonant regions were also included to determine the background. Continuum-continuum coupling was neglected because of its small effect. The required orthogonality conditions of all wavefunctions involved were enforced by Schmidt's recipe. With these wavefunctions in hand, all nonadiabatic coupling matrix elements among discrete states were calculated. Coupling interactions between autodetaching and continuum states were

considered to be due to an electron-electron interaction (i.e., the $1/r_{12}$ term). This calculation involves tedious, non-separable, six-dimension integrations that we carried out numerically. We carefully kept numerical errors within 10^{-6} . The molecular states we included in the calculation are those associated asymptotically with H^- and H states: $H^-(1s^2)$, $H^-(2s^2; ^1S)$, $H^-(2p^2; ^1D)$, $H^-(2s2p; ^1P)$, $H^-(2p^2; ^1S)$, $H(1s)$, $H(n=2)$, and $H(3s)$, plus 40-50 discretized continuum states. A semiclassical molecular-orbital expansion method was employed for collision dynamics calculations, with all possible couplings described above included. The total scattering wavefunction was expanded as a product of a time-dependent expansion coefficient and the discrete or continuum wavefunction. We solved the coupled equations thus obtained numerically to extract scattering amplitudes.

The adiabatic potentials for the HHe^- and $HHe + 1e$ systems are illustrated in Fig. 1. The ground $[H^-(1^1S) + He]$ channel has two avoided crossings with the $[H + He + 1e]$ channel, at intermolecular separations of 0.5 and 2.2 a_0 . Doubly excited states have a strong avoided crossing at 0.4-0.6 a_0 . The $(2s^2)^1S$ and $(2p^2)^1D$ levels lie below the $[H(n=2) + He + 1e]$ channel threshold, while the $(2s2p)^1P$ level is known to be slightly above this threshold. Therefore, this level is called a shape-resonance state. In fact, between the $(2p^2)^1D$ and $(2s2p)^1P$ levels, a large number of Rydberg states occurs. These doubly excited states are known to be strongly correlated.

The calculated EES at an angle of 10° for H^- incident at 1 keV is shown in Fig. 2a. The $(2s^2)^1S$, $(2p^2)^1D$ and $(2s2p)^1P$ levels are clearly identified. Because of strong radial coupling between the ground $H^-(1s^2)$ and excited $H^-(2s^2)$ states at internuclear separation $\cong 0.2 a_0$, $H^-(2s^2)$ formation is dominant at this energy. Formations of the other two levels are also strong because of strong radial coupling from the ground state to the $H^-(2p^2; ^1D)$ state at internuclear separation $\cong 0.3 a_0$. Because of the small energy defects and, correspondingly, the strong couplings among these three doubly excited states, the flux mixes well once the flux is excited into one of these levels, redistributing it among the levels. The main flux transition to the $H^-(2s2p; ^1P)$ state is via the $H^-(2p^2; ^1D)$ state. (The rotational coupling that directly connects H^-

($2s2p;^1P$) and the ground state is secondary.) Furthermore, the $H^-(2s2p;^1P)$ state couples strongly with the $[H(n=2) + He + 1e]$ state; therefore, inclusion of the continuum states associated with this $H(n=2)$ level is essential for a correct description of the dynamics. The structure due to this interference is seen in the calculated result. The energy separation between the ($2p^2$) and ($2s2p$) levels is small, with a splitting energy of 0.04 eV. Hence, the two peaks arising from these channels virtually overlap.

We have carried out other calculations of the EES by varying the ejected-electron angles for energies of 0.5 keV and 10 keV. From these results, we found that the EES shows relatively weak dependence on the incident energy of the H^- . Moreover, because of the weakly repulsive nature of the electron interaction with both the H atom and, in particular, the He atom, the electron charge distribution is enhanced slightly toward the forward angle, resulting in a slight distortion in the observed spectrum, compared to the spectra for photodetachment (18). However, the size of the distortion in the EES is much smaller than that for p and $\bar{p}$ impacts (10), in which the electron cloud of H^- is significantly polarized because of long-range Coulomb interaction. Hence, within our model, we observed a very weak molecular effect, which is consistent with the measurement by Risley (2). As a result, the line shapes near each peak of the ($2s^2$) 1S and ($2p^2$) 1D states mostly reflect the interference effect of the Fano configuration-interaction mixing profile (19); in contrast, the line shape of the ($2s2p$) 1P resonance is due mostly to the shape resonance. Overall, the spectral shapes of the three resonances are very similar to those obtained by electron scattering from the H atom (20). As the collision energy decreases from 1 keV to 100 eV, some characteristics of the EES with respect to the ejected-electron angle might emerge because of increasing sensitivity to details in the molecular structure. This sensitivity also translates into structures seen experimentally in differential cross sections, which we will report in details in a forthcoming paper.

The present spectrum, convoluted with a Gaussian width of 0.2 eV, is displayed in Fig. 2b along with the measured spectrum of Risley (2). The general agreement is satisfactory, and most of the overall features are reproduced, proving the present treatment to be reasonable. As

described above, a large number of Rydberg states lie between the $(2p^2)^1D$ and $(2s2p)^1P$ levels. However, because of weak coupling, their widths are generally quite small, making their effects very weak and thus, unmeasurable at present. Therefore, the experimental peak appears as a single broad peak. The present spectra are shifted a few eV from the corresponding photodetachment spectra (18) because of the transformation to the laboratory frame. The effect of Doppler broadening is considered to be small at this collision energy. The peak positions are shifted slightly between the two results. As described above, the present calculation differs from the best theoretical result by a few percent in asymptotic energy levels, particularly for the $H^- (2s2p)$ state. This difference may be partly responsible for the shift in peak positions. We found that the level of agreement for other results at different ejected-electron angles and energies is nearly equivalent to that of the result discussed here.

In conclusion, we attempted the pure *ab initio* calculation of the EES resulting from collisions of H^- with He in the energy region from 1 keV to 20 keV. The result obtained is considered to be in excellent agreement with a previous measurement by Risley, considering the difficulties in the calculations for the EES and molecular states, as well as the collision dynamics of the present system, which are very sensitive to every detail of each step of the calculation and are computationally demanding. Therefore, we believe that we have successfully established a computational capability for calculating molecular properties that involve continuum states, making possible studies of more model-sensitive physical properties such as double ionization processes. We plan to report on double and single ionization of He by p and $\bar{p}$ impacts in a separate paper.

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References

- [1] J. S. Risley, A.K. Edwards, and R. Geballe, Phys. Rev. Lett. **29**, 904 (1972)
- [2] J. S. Risley, Ph.D. Thesis (1973)
- [3] J. S. Risley and R. Geballe, Phys. Rev. A **10**, 2206 (1974)
- [4] J. S. Risley, Phys. Rev. A **10**, 731 (1974)
- [5] J. Gauyacq, J. Phys. B **13**, 4417 (1980)
- [6] T. S. Wang and J. B. Delos, Phys. Rev. A **29**, 542 (1984); *ibid*, **29**, 552 (1984)
- [7] C. R. Liu and A.-F. Starace, Phys. Rev. Lett. **62**, 407 (1989)
- [8] Y. K. Ho, Phys. Rep. **99**, 1 (1983)
- [9] C. D. Lin, Phys. Rev. Lett. **35**, 1150 (1975)
- [10] K. Hino, M. Nagase, H. Okamoto, T. Morishita, M. Matsuzawa, and M. Kimura, Phys. Rev. XX, XXX (19XX).
- [11] K. Moribayashi, K. Hino, M. Matsuzawa and M. Kimura, Phys. Rev. A **44**, 7234 (1991)
- [12] K. Moribayashi, K. Hino, M. Matsuzawa and M. Kimura, Phys. Rev. A **46**, 1684 (1992)
- [13] M. Kimura and N.F. Lane, Adv. At. Mol. Phys. **26**, 79 (1989)
- [14] H. S. Taylor, Adv. Chem. Phys. **18**, 91 (1970)
- [15] B. Liu, K. Oohata and K. Kirby-Docken, J. Chem. Phys. **67**, 1850 (1977)
- [16] J. N. Bardsley, Case St. At. Phys. **4**, 299 (1974)
- [17] See, for example, N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980)
- [18] M. Halka et al, Phys. Rev. A **46**, 6942 (1992)
- [19] U. Fano, Phys. Rev. **124**, 1866 (1961).
- [20] G.J. Schulz, Rev. Mod. Phys. **45**, 378 (1973)

Figure captions

Fig. 1. Adiabatic potential curves for the HHe^- and $\text{HHe} + 1e$ systems

Fig. 2a. Ejected-electron spectra at 10^0 and 1 keV.

Fig. 2b. Convolutd EES along with the experimental result.

Solid line: the present result. Symbols: experimental results (Ref. 2). The first peak (at 14.5 eV) is due to $\text{H}^-(2s^2)^1\text{S}$, and the second peak (at 15.3 eV) is due to a combination of $\text{H}^-(2p^2)^1\text{D}$ and $\text{H}^-(2s2p)^1\text{P}$.

Fig.1

Fig.2a

Electron energy (eV)