Electron-energy spectra of H⁻ doubly excited states resulting from collisions of H⁻ with He

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Electron-energy spectra for H⁻ doubly excited states resulting from collisions of H⁻ with He are rigorously calculated within a semiclassical molecular representation 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 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 doubly excited states, and identifies the cause of the interference between channels arising from double-electron excitation and direct detachment with simultaneous excitation.

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 the 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 structures 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 and 24 eV, respectively) than does H⁻ (detachment energy, 0.75 eV), thus leading to exceedingly small cross sections for excitation and charge transfer upon a collision; hence, it can safely be treated as an "inert" object in this energy region.

(d) The direct-detachment process, H⁻ + He → H+He +1e⁻, is known to have a large cross section with a magnitude of 10⁻¹⁶ cm² [1–4] and is expected to compete with detachment through doubly excited states, viz., H⁻+He→H⁻**+ He→H⁽*⁾+ He +1e⁻.

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, a 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

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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 paper we report the first rigorous calculation of the electron-energy spectra for H^- doubly excited states resulting from collisions of H^- with He, identify important excitation mechanisms, make the first prediction of the identities of interferences between channels from the direct detachment and detachment through double-electron excitation, and the contributions of $H^-(2p^2;^1D)$ and $H^-(2s2p;^1P)$ states to the spectra. Our theoretical procedures are summarized here; they have been reported previously [13]. A semiclassical molecular-orbital expansion method was employed with a straight-line trajectory for a heavy particle motion. The total scattering wave function $\Psi(t)$ was expanded as a function of the time-dependent coefficient and the molecular discrete $\tilde{\Psi}_\alpha(\mathbf{r}, R)$ or continuum $\tilde{\Psi}_\varepsilon(\mathbf{r}, R)$ state with appropriate phase factors [13] as follows:

$$\Psi(t) = \sum_\alpha a_\alpha(t)\tilde{\Psi}_\alpha(\mathbf{r}, R) + \int d\varepsilon\, a_\varepsilon(t)\tilde{\Psi}_\varepsilon(\mathbf{r}, R) , \qquad (1)$$

where the summation on the right-hand side includes all discrete and doubly excited states and the integral is for continuum states over continuum energy ε. In the present approach, the integral over ε in Eq. (1) was discretized and replaced by the summation of finite-energy meshes. By substituting the total wave function (1) into the time-dependent Schrödinger equation and retaining couplings up to the first order of relative velocity v, one obtained a standard set of first-order coupled equations for scattering amplitudes [13]:

$$i\frac{da_\beta(t)}{dt} = \sum_\beta \mathbf{V}\cdot(\mathbf{P} + \mathbf{A})a_\beta(t) , \qquad (2)$$

where $\mathbf{P}$ represents the nonadiabatic (radial and rotational) coupling and $\mathbf{A}$ denotes the correction arising from electron translation factors. The coupled equations (2) were solved numerically to extract scattering amplitudes subject to the initial condition $a_\beta(-\infty) = \delta_{i\beta}$: the square of the scattering amplitude gives the transition probability.

For discrete states, we adopted the Feshbach projection operator method, in which the Q operator covers the space spanned by both the discrete as well as the doubly excited 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 [14]. The stabilization procedure was adopted to ensure that the desired doubly excited states would be obtained [15]. Slater-type orbitals, employed as a basis set, were taken from Ref. [16], 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 [17]. 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 [18]. The asymptotic energy levels we obtained are within 0.2%, 0.6%, 2.3%, and 4.6% of the best available theoretical results [8] for the ground $H^-(1s^2)$, $H^-(2s^2)$, $H^-(2p^2;^1D)$, and $H^-(2s2p;^1P)$ levels, respectively. These are considered to be 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 [19]. The continuum states [the second term in Eq. (1)] were properly discretized by using energy samplings based on the Gaussian quadrature [20]. All of the 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 wave functions involved were enforced by Schmidt's recipe. With these wave functions in hand, all nonadiabatic coupling matrix elements among discrete states were calculated. Coupling interactions between doubly excited and continuum states were considered to be due to an electron-electron interaction (i.e., the $1/r_{12}$ term). This calculation involves tedious, nonseparable, six-dimensional 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. All possible couplings described above were included in dynamical calculations which solved the coupled equations (2).

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 $0.5a_0$ and $2.2a_0$. Doubly excited states have a strong avoided crossing at $0.4–0.6a_0$. 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 occur. 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. 2(a). 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 $\simeq 0.2a_0$, $H^-(2s^2)$ 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
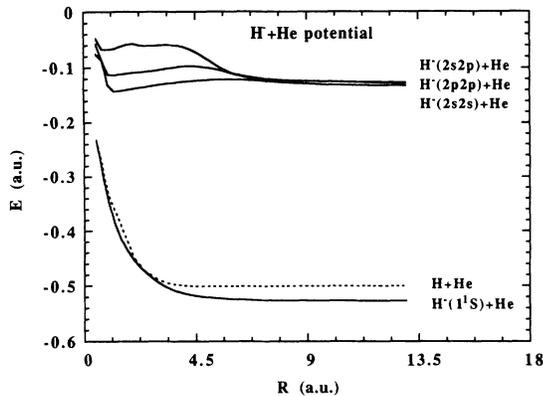
FIG. 1. Adiabatic potential curves for the HHe^- and $HHe + 1e$ systems.

$H^-(2p^2;^1D)$ state at internuclear separation $\simeq 0.3a_0$. 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
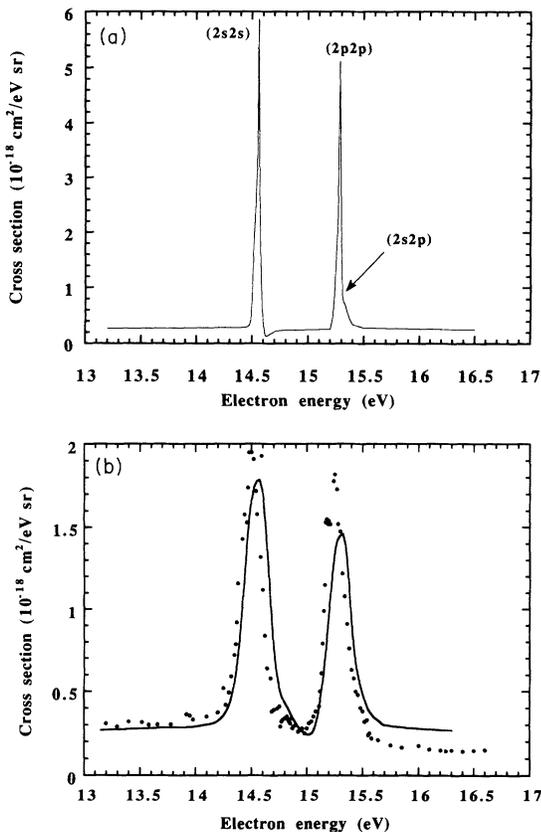
FIG. 2. (a) Ejected-electron spectra at 10° and 1 keV. (b) Convoluted EES along with the experimental result: Solid line, the present result; symbols, experimental results [2]. The first peak (at 14.5 eV) is due to $H^-(2s^2;^1S)$ and the second peak (at 15.3 eV) is due to a combination of $H^-(2p^2;^1D)$ and $H^-(2s2p;^1P)$.

$H^-(2p^2;^1D)$ 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 $[H(n=2)+He+1e]$ states, i.e., direct detachment with a simultaneous excitation 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 $(2p^2)^1D$ and $(2s2p)^1P$ 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 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 [21]. 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 [22]; 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, as expected, very similar to those obtained by electron scattering from the H atom [18]. 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 detail in a forthcoming paper.

The present spectrum, convoluted with a Gaussian width of 0.2 eV, is displayed in Fig. 2(b) along with the measured spectrum of Risley [2]. The general agreement is satisfactory, and most of the overall features are reproduced, proving that the present treatment is 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 [21] 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 experimental and present results. As described above, the present calculation differs from the best theoretical result by a few percent in asymptotic energy levels, particularly for the

$H^-(2s2p;^1P)$ state. This difference may be partly responsible for this 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 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.

[1] J. S. Risley, A. K. Edwards, and R. Geballe, Phys. Rev. Lett. **29**, 904 (1972).

[2] J. S. Risley, Ph.D. thesis, University of Washington, 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); **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. A **49**, 3753 (1994).

[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. Sato and S. Hara, J. Phys. B **13**, 4577 (1980); T. F. O'Malley and S. Geltman, Phys. Rev. **137**, 1344 (1965).

[15] H. S. Taylor, Adv. Chem. Phys. **18**, 91 (1970).

[16] B. Liu, K. Oohata, and K. Kirby-Docken, J. Chem. Phys. **67**, 1850 (1977).

[17] J. N. Bardsley, Case Stud. At. Phys. **4**, 299 (1974).

[18] G. J. Schulz, Rev. Mod. Phys. **45**, 378 (1973).

[19] See, for example, N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980).

[20] M. Kimura and N. F. Lane, Phys. Rev. A **41**, 5938 (1990).

[21] M. Halka et al., Phys. Rev. A **46**, 6942 (1992).

[22] U. Fano, Phys. Rev. **124**, 1866 (1961).