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The Negative Ion of Hydrogen

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Abstract. The negative ion of hydrogen continues to be important in atomic physics and astrophysics. Correlations between the two electrons are strong already in the ground state, the only bound state in this three-body system. This state attracted early interest, especially for the description of stellar atmospheres by Chandrasekhar and others. More recently, the rich spectrum of doubly-excited states, and the nature of the double escape above the break-up energy of 14.35 eV, have been central to our understanding of highly-correlated, non-separable problems in quantum physics. This article is a survey of the story of H^- as it has developed over the last seventy years.

1. Prologue

This is primarily the story of a negative ion, offered as a tribute to the memory of a great astrophysicist who contributed to its early understanding. It is also a personal account because both the negative ion, H^-, and the astrophysicist, S. Chandrasekhar, have had major influences on my own career in physics. I begin, therefore, on that personal note.

In common with many an Indian student over the past several decades, Prof. Chandrasekhar's immense contributions to physics and astrophysics and his stature in the scientific world were an inspiring attraction and motivation as I made my own early decisions to enter the field. I first saw and heard him when he delivered a lecture at the University of Delhi in the early 1960s while I was an undergraduate student there. Later, in my decision on a graduate school, his presence on the faculty was one of the determinants in my choosing the University of Chicago. He was just beginning his work in the field of General Relativity and, although I chose to work for my thesis in another field and under another Faculty Advisor, I took almost every course that he taught during my graduate school years. However, his generally stern and serious manner meant that our interactions were confined to the classroom.

Only in my last year at Chicago did I go further, daring to seek time for conversations in his office on topics in my research having to do with H^- that I felt sure would interest him. That step set the stage for what became my standard practice in all subsequent visits to Chicago over the next 12–15 years, to call on him at his office. Very conscious of his dislike of small talk and of his intense focus, I always felt the need to go in with some scientific item to discuss but, depending on the mood and the interchange, these conversations ranged broadly over physics and philosophy, with his ideas and opinions about them and about the physicists he had known. On many of these occasions he was in a relaxed mood, wanting to talk about some subject, sometimes for long periods. I can still see his smile and hear his characteristic "consequently" as he made a point. These conversations remain among my most memorable experiences in my life in physics. I note one of possible general interest. I had become fascinated with the principle of invariant imbedding and had worked on it for problems in atomic scattering. Since he and Ambartsumian had launched the subject of what he called "the principles of invariance", I went in on one of these visits to tell him about some of my results. During that conversation, he said that of all the work he had done, many were much more difficult and complicated but the one that "gave the greatest satisfaction" was his work on the principles of invariance, that he found during the course of that work that the subject had "its own natural flow, each step following inevitably the previous one, nothing forced".

Chandrasekhar's presence there led me to the University of Chicago although not to doing research under his supervision. But I fell in with H^- and am still involved in understanding this two-electron system more than twenty-five years later. Although a simple system, indeed the simplest non-trivial problem in the study of atoms and ions, and one that has been studied since the earliest days of quantum mechanics, it continues to pose challenges to our theoretical understanding. The story of H^- is rich in physics and is far from being closed. It is the prototypical three-body system in atoms and, therefore, the system of choice for studying the intricacies of three-body dynamics in a quantum system. With long-range Coulomb interactions between all three pairs of particles, the dynamics is particularly subtle in a range of energies that lie roughly 2 – 3 eV on either side of the threshold for break-up into proton + electron + electron at infinity. In this energy range, there is a delicate balance between the attractive and repulsive interactions and, given the low kinetic energies involved, the particles develop strong correlations in energy, angle and spin degrees of freedom. Perturbation and other conventional techniques fail, posing a challenge to our mathematical and physical understanding. At the same time, such understanding can be expected to apply broadly to all correlations in multi-electron atoms and elsewhere in physics as well. Just as the hydrogen atom is not only the prototype of all one-electron atomic physics but lends its basic ideas, notation, and terminology to other realms, whether excitons and heterostructures or quarkonium, so also will the understanding of H^- apply to and become part of our intuition about coupled, non-perturbative, strongly correlated systems throughout physics.

Further, H^- has been important in the study of our atmosphere (particularly, the ionosphere's D-layer) and even more, of the atmosphere of the Sun and other stars, as first documented by Chandrasekhar, and it has also been central to the development of accelerators, being the ion of choice to start with even when one is interested down the line in beams of protons, mesons or neutrinos.

2. Early history: the ground state

Current research on the strong electron-electron correlations displayed by H^- concentrates on the energy range of high excitation of both electrons but the early focus, both in physics and in astrophysics, was on the ground state of this negative ion. Indeed, H^- is peculiar in that, unlike with other members of the two-electron isoelectronic sequence, correlations between the electrons are crucially important from the start, even in the ground state. This is not surprising because He, Li^+ and other members of this sequence, have a dominant Coulomb attraction by the nucleus for both electrons, the interaction between the electrons being perturbative in comparison, so that perturbation and variational methods suffice to give a good description of the binding energy of the ground and low-lying excited states. In H^- on the other hand, this is no longer true. As is well known from the earliest days, a simple Hartree self consistent field treatment with each of the 1s electrons seeing an effective charge, $Z_{\text{eff}}= Z— 5/16$, gives a very accurate value of the ground state energy for all $Z \geq 2$ but fails completely for H^- The predicted variational energy of $–(11/16)^2$ atomic units (1 a.u.=27.21 eV), lies above the ground-state Bohr energy of –1/2 for H, so that one cannot even conclude that H^- is a bound entity relative to (H + electron at infinity).

It was not till Bethe's 1929 paper, therefore, that there was unambiguous proof of the existence of H^- as abound system (Bethe 1929). Using the Hylleraas variational wave functions which involve the three coordinates, $s \equiv r_1+ r_2$, $t \equiv r_1 - r_2$, and $u \equiv r_{12}$, Bethe employed a three-parameter $\{\alpha, ß, k\}$ function of the form $(1 + \alpha u + ßt^2) \exp(- ks)$ to conclude for the first time that the resulting Rayleigh-Ritz upper bound on the energy lies below –1/2 a.u. The presence of the term in αu, involving explicitly the inter-electronic distance, speaks to the necessity of including correlations to arrive at such a conclusion. Soon after, Hylleraas, who had pioneered similar calculations for He and higher members of the two-electron sequence, also arrived independently at the same conclusion, his six-parameter calculations giving of course a slightly lower energy (Hylleraas 1930). Today, later generations of such calculations, most notably by Pekeris, Kinoshita and the others who have followed them (cf. Koga & Matsui 1993; Koga & Morishita 1995), employ hundreds of parameters to give the binding energy of H^- to many-decimal accuracy. These variational calculations have even become a canonical test of new numerical procedures and of the speed and capacity of new generations of computers, the value of (approx.) 0.75 eV for this binding energy being a number remembered by most atomic physicists and astrophysicists.

While many-parameter variational calculations give the ground state energy of H^- to great accuracy, the best experimental values come from a high resolution (0.03 cm) laboratory photodetachment experiment with lasers. Extrapolating with the use of the known threshold behaviour for this detachment (to be discussed further below in section 2.1), the threshold and thereby the electron affinity (or binding energy) has been determined to be 6082.99 ± 0.15 cm^{-1} for H(F=0) and 6086.2 ± 0·6 cm for the similar D (F = 1/2) states (Lykke *et al.* 1991).

2.1 *Opacity of stellar atmospheres*

The astrophysical importance of the existence of a weakly bound H^- was first recorded in the literature by Wildt (1939, 1941). The abundant presence of both hydrogen and low energy electrons in the ionized atmospheres of the Sun and other stars argues for the formation of H^- by electron attachment. At the same time, subsequent photodetachment back to H^+ electron for photon energies larger than 0.75 eV points to its importance for the opacity of these atmospheres to the passage of electromagnetic radiation. Indeed, since most neutral atoms and positive ions have their first absorption at 4 or 5 eV if not larger, H^- is the dominant contributor to the absorption of 0.75 – 4 eV photons, a critical range of infrared and visible wavelengths. At this point, Chandrasekhar played a crucial role in the subsequent story of H^-, both in physics and astrophysics. The continuum absorption coefficient in the solar atmosphere as a function of wavelength was well-known. As shown in figure 31 of his book (Chandrasekhar 1960), it increases by a factor of two from 4,000 to 9,000Å, then decreases to a minimum at 16,000Å, followed by another increase. It was also known that this shape is characteristic of many other stars with surface temperatures less than 10,000 K. For a long time, until Wildt's suggestion, people had tried to explain this shape as due to continuous absorption by H or some of the other abundant species such as Na, Mg, Ca, Fe and Si, but the wavelength dependence did not match. Following Wildt, it became natural to look to H^- for the explanation, but attempts and calculated absorption coefficients by Jen, Massey and Bates, Williamson, Wheeler and Wildt, etc., were unsatisfactory, as pointed out by Chandrasekhar.

Fig. 1 drawn from Bethe and Salpeter (1977) shows the very different shapes of the photoabsorption of a negative ion as compared to neutral atoms. Simple physics underlies this difference. Following photoabsorption by H^-, the photoelectron departs in a *p*-wave. Just above threshold, the low energy electrons see the angular momentum barrier as the longest-range potential and their tunneling through the barrier suppresses the cross-section. Therefore, as seen in the figure, the cross-section rises from zero, following the Wigner $E^{l+1/2} = E^{3/2}$ law (Wigner 1948). It later rises to a peak value and then gradually falls off. In contrast, photoionization of neutral atoms behaves quite differently. The longest range potential for the photoelectron is now an attractive Coulomb one which has two effects. It enhances the wavefunction near the origin and it also renders l irrelevant since the angular momentum $1/r^2$ potential falls off faster than the Coulomb. The net effect is that photoionization cross-sections are independent of the l-value of the photoelectron and start at a finite value at threshold, to fall off in some fashion at higher energies (cf. Rau 1984a). It is the difference in shapes and, in particular, the feature of a broad region of absorption somewhat above threshold that makes H^- important for stellar atmospheres in the 4,000 20,000Å wavelength range. Next, for quantitative treatment, Chandrasekhar appreciated the special features associated with its weak binding.

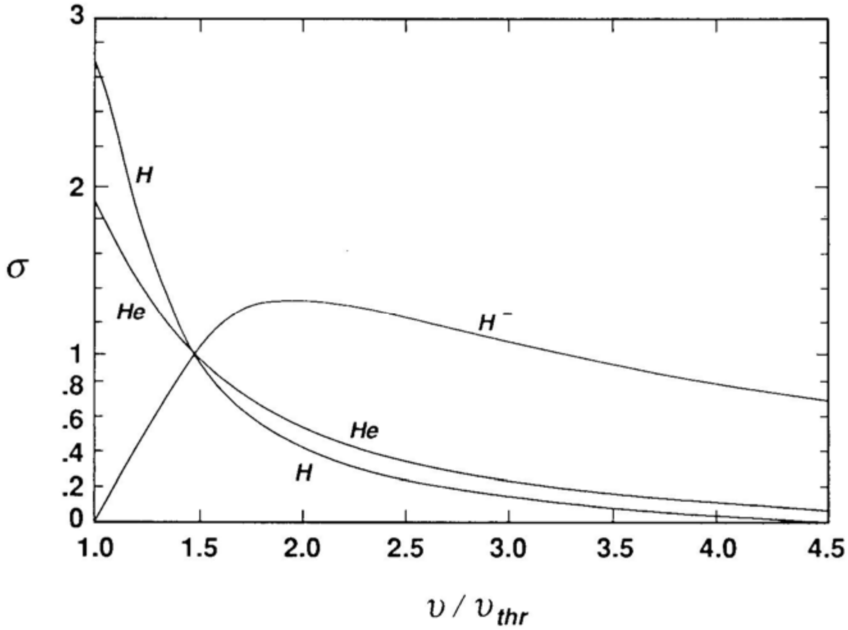

Figure 1. Contrast between the cross-section for photoionization of neutral atoms and photodetachment of a negative ion. Horizontal axis is the incident photon frequency in units of the threshold frequency (from Bethe & Salpeter 1997).

2.2 *Compensating for errors introduced by a diffuse wave function*

It is now common wisdom that Rayleigh-Ritz variational calculations may provide accurate energies while the wave function itself may be seriously deficient in other regards. This is particularly important for a weakly bound system such as H^- with its very extended wave function. Together with the deuteron, H^- is a canonical example of a loosely bound quantum system wherein the wave function and probability amplitude can extend beyond the range of the binding potential itself. Chandrasekhar & Krogdahl (1943) pointed out that for the matrix element in the photoabsorption coefficient, the wave function at distances of 4 – 5 a_0 (Bohr radius, $\simeq$ 0·53Å) is involved and even a many-parameter function may give a poor description at this distance while providing a reasonable energy (which arises more from the wave function at smaller r). As a result, they argued that trial functions be subjected to sum rule tests as indicators of their reliability. Together with the Thomas-Reiche-Kuhn total oscillator strength sum rule, they developed another which related the integrated continuum absorption coefficient to the matrix element of r^2, this sum rule following from the assumption that H^- has only one bound state. This too is an interesting element of the H^- story. For one-electron excitations, a negative ion is very different from its higher isoelectronic analogs. Unlike the infinite number of bound excited states in positive ions and neutral atoms, negative ions have a much sparser spectrum. A rigorous proof that H^- has only one bound state, the ground state, and no singly excited states at all is very recent (Hill 1977 a,b) but not unexpected from the earliest days. Chandrasekhar thanks E. Teller for a conversation regarding his assumption that there are no excited bound states.

Based on these sum rules and under Chandrasekhar's influence, Henrich (1944) did a 11-parameter Hylleraas calculation for H^-. The next important step was taken a year later when Chandrasekhar, pursuing the same theme that the wave functions may be poorer at large r, developed alternative forms of the photoabsorption matrix element (Chandrasekhar 1945). Today these have become standard in our thinking but they first appeared in this context, with Chandrasekhar pointing out that the usual "dipole-length" form of this electromagnetic coupling, $\vec{e}\varepsilon\ \vec{r}$, weights large values of r, precisely where the H^- functions are deficient. But through commutation relationships involving the Hamiltonian, an alternative can be developed which involves matrix elements of the momentum operator p. Another alternative gives an "acceleration" form and even more alternatives are of course possible. The "momentum" form (today more often called "dipole-velocity") weights the same small -r regions which contribute most to the energy. The wave function in that region being, therefore, expected to be more reliable, the "momentum" calculation of the absorption coefficient may by the same token be more trustworthy. In this vein, Chandrasekhar & Breen (1946), working with the Henrich 11-parameter function, showed that the H^- photoabsorption does indeed peak at 8,500Å and that H^- can itself account for the continuum absorption coefficient in the solar atmosphere over the entire range from 4,000 to 25,000A [as in figures 3 and 4 of Chandrasekhar & Breen (1946) and figure 32 of Chandrasekhar (1960)]. Characteristic of Chandrasekhar's work at other times and on other problems, they presented extensive tables and, in a succeeding paper with Münch (Chandrasekhar & Munch 1946), applications were made to all A0 – G0 stars. (As an aside, there is no general rule that the velocity form of the dipole matrix element is always superior. Indeed, one of my first conversations with Chandrasekhar grew from my analysis (Rau & Fano 1967) that the asymptotic form of a transition matrix element at high momentum transfer was better described by the length form).

2.3 *Radial correlation and a simple wave function*

The above works are notable for their contribution to atomic physics of alternative forms of the photoabsorption matrix element and to astrophysics of a complete accounting of the opacity of stellar atmospheres. For these detailed quantitative applications, he used many-parameter Hylleraas functions (as also in later work (Chandrasekhar & Herzberg 1955) on He, Li^+ and O^{6+}) but another paper of Chandrasekhar's around this time is notable for a further important insight into the structure of H. He introduced a two-parameter trial wave-function,

$$\exp\left(-\alpha r_1 - \beta r_2\right) + \exp\left(\alpha r_2 - \beta r_1\right), \tag{1}$$

and showed that the energy minimum at α =1.03925 and β= 0.28309 is sufficient to provide binding for H^- (Chandrasekhar 1944). There is no explicit use in (1) of the electron-electron correlation, only the imposition of the Pauli symmetrization requirement for this ^1S function which differs from the Hartree or Hartree-Fock one parameter wave function wherein $\alpha = \beta = Z_{\text{eff.}}$ The function in (1) is, therefore, referred to sometimes as an “unrestricted” Hartree-Fock function, the two 1*s* electrons not restricted to see the same effective charge and, therefore, to have the same orbital. The function exhibits a radial “in-out” correlation between the electrons such that when one electron is “in” close to the nucleus, the other is kept “out”. Particularly striking is the feature that α is larger than 1, so that the presence of the second, “outer” electron pushes the inner one closer to the nucleus than it would be were it alone bound to the proton. Thereby it “sees” an effective charge larger than the value unity of the proton’s real charge! At the same time, the outer electron also sees enough of an effective charge, albeit small, to be itself bound. In the same paper, Chandrasekhar also considered a second function which included an additional factor $(1 + cr_{12})$ in (1) which, of course, improved the binding energy and indeed was superior to the 3-parameter Bethe-Hylleraas result. See Bethe & Salpeter (1977) for other discussions on the ground state of two-electron atoms and ions. For recent reviews on negative ions, see Bates (1990) and Buckman & Clark (1994).

The Chandrasekhar function (1) shows the specific nature of electron-electron correlation in the ground state of H^- Of the two kinds of correlations, “angular” between the directions $\hat{r}_1$ and $\hat{r}_2$ and “radial” between the magnitudes r_1 and r_2, it is the latter that proves crucial. Further, the two electrons are on a very different footing, one bound much closer to the nucleus than the other which is weakly held at a distance $\simeq 4 - 5\ a_0$ from the nucleus. This suggests a very useful next step, of regarding photoabsorption and other collision processes as primarily due to this electron so that a “one-electron picture” of H^- suffices, this electron regarded as weakly bound in a short-range attractive potential well. An extreme model takes the attraction to be of “zero-range” (or, indeed, as a delta-function well) so that a single parameter, the binding energy, characterizes the form of the wave function of the outer electron as $\exp(-k_B r)\ /r$, where $\frac{1}{2}k_B^2$ is the electron affinity of H^- ($\simeq 0.75$ eV). Together with a constant C that allows for normalization, and takes the numerical value 0.31552, Ohmura & Ohmura (1960) took the resulting two-electron wave function

$$(1/2)^{1/2}(1 + P_{12})\,\Psi_0(r_1)\,C\exp(-k_B r_2)\,/r_2, \tag{2}$$

where P_{12} is the particle interchange operator, and evaluated the continuum photoabsorption coefficient shown in fig. 2. This calculation, which describes the outgoing photoelectron by a free *p*-wave, is extremely simple and completely analytical, while giving a very good description of the absorption coefficient over the entire range from 4,000 to 16,000Å (section 7.2.4 of Fano & Rau 1986). Figure 2 is a re-rendering of the H^- curve in Fig. 1 and similar to equivalent figures in Chandrasekhar’s papers that were referred to in section 2.2.

Besides photodetachment, collision processes involving H^- are also important

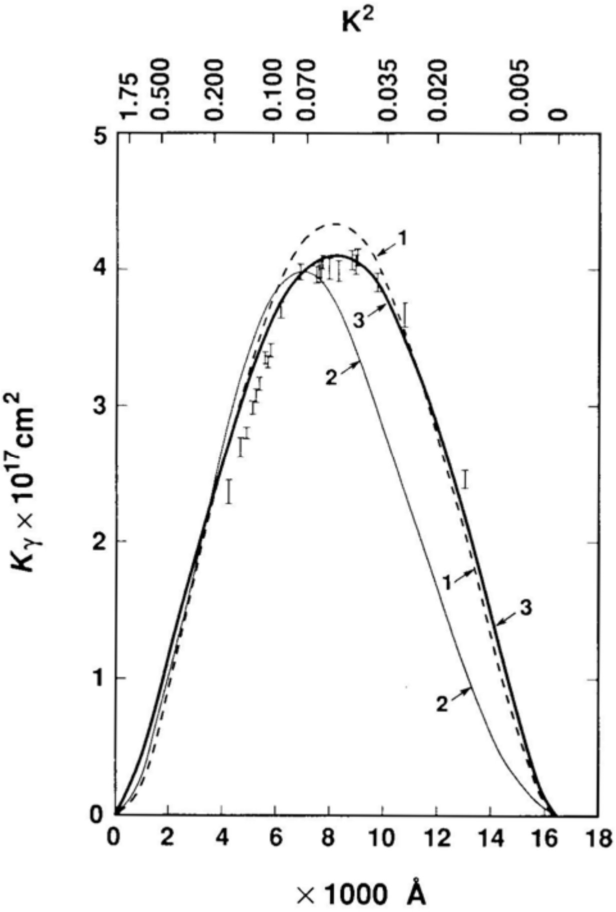

Figure 2. Continuous photoabsorption coefficient of H^- from Ohmura & Ohmura (1960). Data from experiment compared with the analytical expression from the simple "zero-range wave function" in (2), plotted as curve 3, and with numerical results using a 20-parameter Hylleraas variational wave function in curves 1 ("dipole velocity" form) and 2 ("dipole length" form). Horizontal axes are in photon wavelength (bottom) and photoelectron energy in Ry (top).

in stellar atmospheres. Prominent among these are collisions with the neutral hydrogen and protons that are abundantly present. One among the many results is that "charge exchange", $H + H^+ \rightarrow H(1s) + H(nl)$, dominates over "associative detachment", $H^- + H \rightarrow H_2 + e$, in atmospheres with temperatures greater than 8,000 K and in lower temperature stars with lower surface gravity (cf. Praderie 1971).

3. One-electron excitations

The very weak binding already of the ground state, and the absence of a long-range Coulomb attraction for the outer electron, make the excitation spectrum of H$^-$ very different from He and higher members of the isoelectronic sequence. As already noted, there are no other bound states at all (except for an item to be mentioned in section 4.5), no counterparts of the multiple infinity of Rydberg states in He. The only excited states are, therefore, of the one-electron continuum of (H$^+$ electron) which begins 0·75 eV above the H$^-$ ground state. These are, of course, the same states involved in elastic scattering of low energy (< 10 eV) electrons from ground state hydrogen. They have also played an important role as tests of our understanding of electron-atom scattering; see, for instance, a recent review on electron-H scattering (Bray & Stelbovics 1995). Proper treatment of exchange, the singlet and triplet scattering lengths being very different, and of the polarizability of the H ground state (which leads to an attractive r^{-4} potential seen by the scattered electron), are important in describing this scattering. An early variational calculation by Schwartz (1961), with over fifty parameters in the wave function, continues to serve as a benchmark against which later calculational techniques and numerical values are sized up.

As noted in section 2.2, although it was suspected from the beginning that there may be no excited 1 *snl* bound states of H$^-$, nevertheless there were temptations from time to time to attribute unexplained diffuse interstellar lines to such states. In the 1950s and 1960s, such suggestions were made with regard to absorption lines at 4,430, 4,760, 4,890 and 6,180Å. Given the persistence of these speculations and their astrophysical significance, a careful laboratory laser photodetachment experiment by Herbst *et al.* (1974) finally demonstrated conclusively that there is no structure in the detachment cross-section at these wavelengths. As already noted, today we have a completely rigorous mathematical proof (Hill 1977a,b) that there are no one-electron excited bound states of H$^-$.

3.1 *Excitation in static electric and magnetic fields*

With the interaction of photons below 10 eV with H$^-$ essentially understood, more recent work has turned to the effect of additional external electromagnetic fields. Considering first static fields, both electric and magnetic fields are of interest. In both situations, for laboratory field strengths of interest, the couplings $e\vec{\varepsilon}\,\vec{r}$ and $(e^2B^2/8mc^2)r^2\sin^2\theta$ (from the quadratic or diamagnetic coupling) share the common feature of being negligible at small r and increasing with radial distance. To an excellent approximation, therefore, they affect only the final state of the detached photoelectron and that too only at large distances. The initial state of H$^-$ and the initial absorption of the photon by it are essentially unchanged from the zero-field case. Only the large-r wave function of the photoelectron has to be recast in terms of the eigenstates of a free electron in the external potential and these are well known, Airy functions and Landau functions, respectively. The cross-section

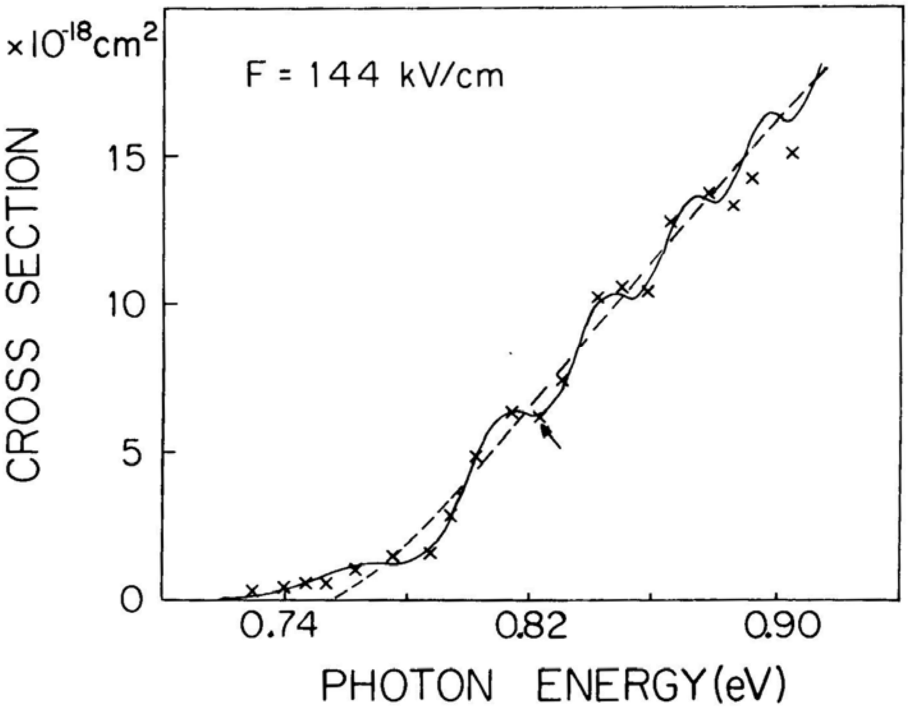

Figure 3. Photodetachment of H$^-$ just above the detachment threshold at 0.75 eV (dashed line) and in the presence of a strong electric field F (solid line). Note in the latter that absorption sets in "below threshold" because of field-assisted tunneling through the sloping potential cFx and that field induced modulations appear at higher energies. The arrow marks the data point that was normalized to the theoretical expression (from Rau and Wong 1988).

for photodetachment in the presence of the external field *F* takes, therefore, a simple form

$$\sigma(F) = \sigma(F = 0)\mathrm{H}_F(k) \tag{3}$$

where $\mathrm{H}_F(k)$ is a "modulation factor" which depends on the outgoing electron's momentum *k*. Simple analytical expressions for this factor have been developed (Greene 1987; Rau & Wong 1988; Du & Delos 1988). In the case of an external static electric field, experimental data is available (Bryant *et al.* 1987) for fields of 10^5 V/cm and, as shown in fig. 3, are in excellent agreement with theoretical calculations (Rau & Wong 1988). Note that photoabsorption sets in below the zero-field threshold energy of 0.75 eV because of field-assisted tunneling and that above this energy, the cross-section displays oscillations about the zero-field cross-section.

It is worth taking note of the experiment that gave the results in fig. 3. Taking advantage of the fact that most particle physics accelerators that accelerate protons start with H$^-$ as the initial species because it has the same mass and magnitude of the charge and the two electrons can be stripped off after acceleration, a group has conducted a series of detailed studies of H^- over the last twenty years at the LAMPF accelerator in Los Alamos (see a review: Bryant *et al.* 1981). The relativistic nature of the 800 MeV H^- beam has been cleverly exploited to make certain measurements that are not otherwise easily carried out. Thus, in the context of Fig. 3, such large electric fields were realized by imposing a modest magnetic field of 10 Gauss on the H beam as it was photodetached by a laser (Bryant *et al.* 1987). This laboratory magnetic field transforms in the rest frame of the H^- beam into both a comparable magnetic but also into a large electric field.

3.2 *Multiphoton detachment*

In recent years, intense lasers have made it possible to observe effects of multiphoton absorption by atoms and ions. Among notable effects are "above-threshold ionization wherein more photons are absorbed than are necessary to break up the system, the extra energy going to increase the kinetic energy of the ejected photoelectron by multiples of the photon energy. The Los Alamos H^- beam mentioned above in section 3.1 has also been used for similar studies of "above-threshold detachment" (Tang *et al.* 1989, 1991). With a CO_2 laser beam of laboratory photon energy 0.117 eV, the relativistic Doppler shift makes it appeal" in the frame of H^- as of energy 0.08 to 0.39 eV, depending on the angle between the photon momentum and the H beam. Detachment, which requires 0.75 eV, takes place therefore as the result of the absorption of two to nine photons or more. Thereby multiphoton detachment and above-threshold detachment have now been experimentally studied in H^- : Fig. 4. Theoretically, this problem had been investigated earlier and by several groups, again primarily because the negative ion is a simpler system than an atom with its Coulomb field and spectrum (cf. Crance & Aymar 1985; Arrighini *et al.* 1987; Geltman 1990 & 1991; Liu *et al.* 1992; Laughlin & Chu 1993; and the collection Gavrila 1992). The coupling of an intense time-dependent electromagnetic field to an atom is still an unsolved problem because neither the external field nor the internal binding field can be treated perturbatively. With a negative ion, especially in a zero-range description as in section 2.3, the internal field is at least simple and, therefore, H has been a system of choice for the study of such time-dependent problems (Gavrila 1992; Wang & Starace 1993).

4. Two-electron excitations

Although H^- is very different from He as regards the one-electron excitation spectrum, they are on the same footing when it comes to states in which both electrons are excited. Indeed, upon regarding them as two excited electrons around a positive charge, H_-, He, Li_+, ... , are exact "iso-double-electronic" analogs, differing only in the magnitude of Z, the central positive charge, $Z = 1, 2, 3, \ldots$. Therefore, as a prototype for the study of doubly-excited atomic states, H^- is as good a candidate as He. Fig. 5 is a sketch of the entire spectrum of H for $L = S = J = 0$, that is, ^1S_e states. Similar sketches describe states of other L, S and J. Fig. 5(a) provides

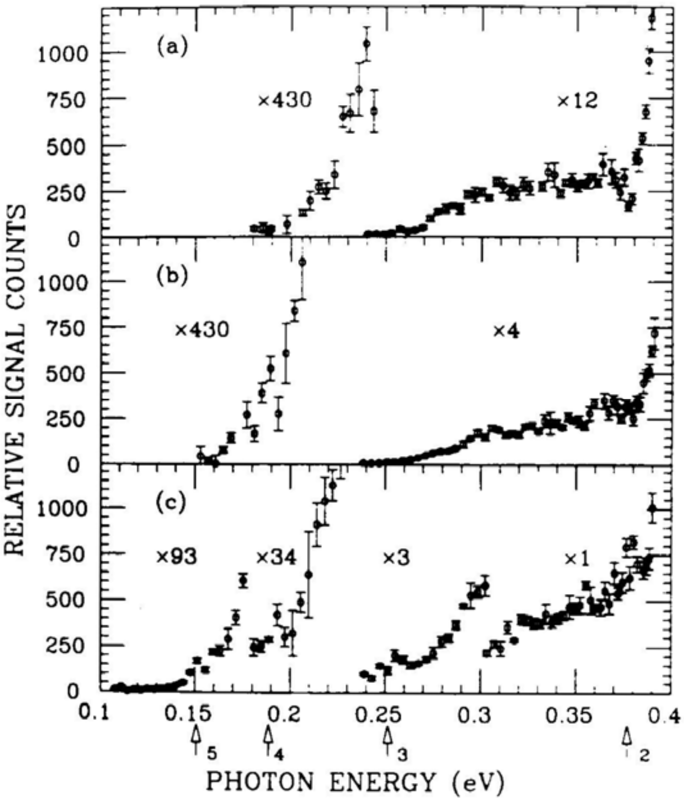

Figure 4. Multiphoton detachment of H^- at different laser intensities: (a) 4 GW / cm^2, (b) 6 GW / cm^2, and (c) 12 GW / cm^2. Multiplication factors indicate the magnification in signal counts (from Tang *et al.* 1991).

the conventional independent-electron labeling, each group of states described as $H(N \geq 2) + e(n \geq N)$. Note N Rydberg series of states (described as l^2 with $l = 0,1, ..., N - 1$) below each single ionization limit, H(N)+ electron at infinity, along with their associated one-electron continuum above this limit. The first group below N = 2 lies, therefore, in the vicinity of 10.95 eV above the ground state of H^-. For analogies to quark families, see Rau (1992).

These states in which both electrons are excited out of the ground 1*s* orbitals are not strict bound states, even in the absence of coupling to the radiation field. This is clear from fig. 5 since these states are degenerate with one or more continuum states of electron plus H (lower N). Thus, the $1/r_{12}$ interaction itself mixes all these degenerate states and the physical eigenstates of the Hamiltonian are superpositions of both, with bound and continuum character. They are quasi-bound, “autoionizing” states (cf. sections 10.1 and 10.2 of Fano & Rau 1986). In a descriptive picture, were one to excite both electrons in H^- to one of the states in fig. 5(a), one electron can drop back into abound state of hydrogen with lower N, the other then ending up with that released energy which is sufficient to let it escape to infinity (“autoionization”).

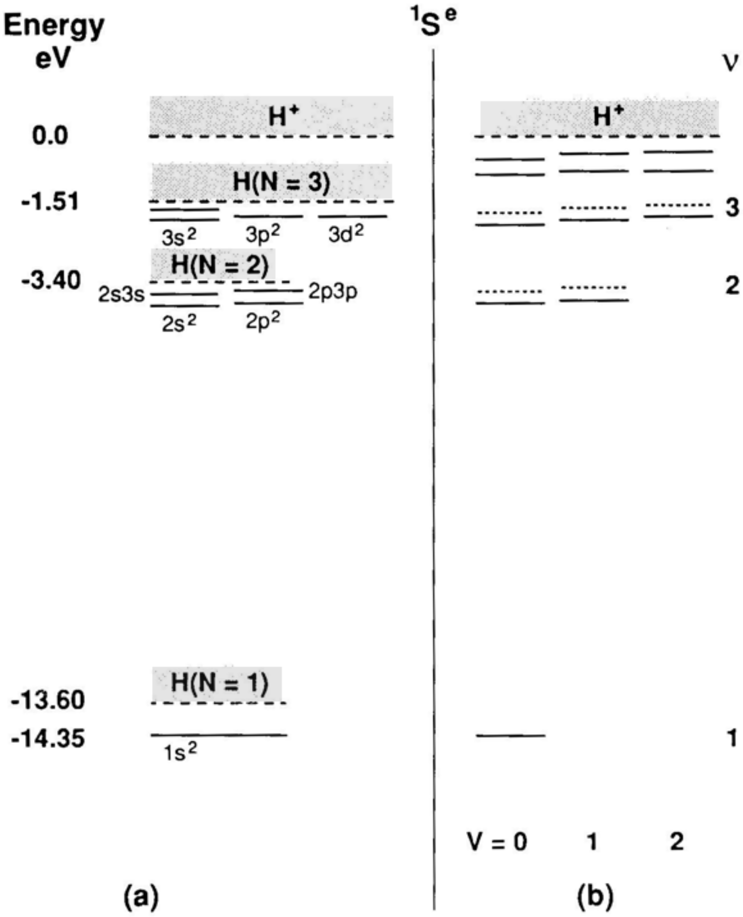

Figure 5. Spectrum of ^1S states of H^- .(a)In independent electron labeling with Rydberg series $|Nl,\ nl\rangle$ converging to states of H(N) plus one electron at infinity. Note the single bound state $1s^2$ of H^- but a rich spectrum of doubly-excited states, with both N and n larger than 1. (b) In a pair labeling, with principal quantum number v, angular correlation number v, and radial correlation number η(= 0, – ; = 1,---; etc.). States with same υ and η form "pair-Rydberg" series converging to the double-detachment threshold of H $_+$ (ee) pair at infinity.

These states manifest themselves as resonances in electron-hydrogen scattering, as for instance, in the elastic scattering of 10.2 eV electrons from the ground state of hydrogen They are also seen in photodetachment of H^- in a corresponding energy range. This range being, approximately, 10.95 – 14.35 eV, energies not easily available with laboratory lasers, it was once again the Los Alamos experiment that provided laboratory studies of these doubly-excited states.

4.1 *Experimental observation*

One of the clever exploitations of a relativistic H^- beam is to use the Doppler effect to tune the laser frequency as seen in the frame of the H^-. By changing the angle a between the two beams, a laboratory frequency von appears to the $H^—$ as v= gv_0(1 + *b* cos a), where *b* ≡ *vlc* and g ≡ (1 —b^2)$^{-1}$/^{2}. In the Los Alamos experiments, v/v_0 could be adjusted from 0.293 to 3.413. As a result, the fourth harmonic of a Yag laser with hv_0 = 4.66 eV can be used to cover the region of doubly-excited states in H^- from 10 to 15 eV (Bryant *et al.* 1981). Small changes in a provide for the tuning, allowing experimental resolution (mainly limited by $H^—$ beam stability) of a few meV. It is worth noting the interesting combination of circumstances that speaks eloquently to the unity of physics. An 800 MeV $H^—$ beam at an accelerator built for studies of mesons and neutrinos is used to study details of an atomic state around 10 eV with a few meV accuracy! The resulting photodetachment cross-section is shown in fig. 6 and represents an extension of fig. 2 to higher energies (Broad & Reinhardt 1976).

Against a background of the one-electron continuum absorption, doubly-excited states of H^- appear in fig. 6 as groups of resonances in the vicinity of the various single ionization limits H(N) — see fig. 5. Selection rules for single photon absorption by the ground $^I S^e$ state lead to $^1P^o$ states, the lowest such doubly-excited states being the ones associated with H(N = 2) and loosely termed 2*s*2*p*. Experimental data in fig. 7 show in greater detail that there are two prominent resonances, a sharp one just below the N = 2 threshold at 10.95 eV above the ground state and a broader one just above that threshold (Bryant *et al.* 1977). Similar sets of resonances have been resolved in the experiment below higher N up to N = 7, fig. 8 providing as an example the N = 5 set (Harris *et al.* 1990). Although the integrated oscillator strength over the resonances may be small compared to the background continuum, the resonance structures are dramatic over the narrow energy ranges where they occur. Although they have not been observed or discussed so far in the astrophysical context, the advent of far-ultraviolet telescopes may well make them relevant for future studies of stellar atmospheres in this wavelength range of 900 – 1,100A.

4.2 *Strong correlations*

Once both electrons are excited away from the nucleus, correlations between them become more important. In H^-, as already noted, radial correlations are already important in the ground state but, whether in H^- or He, radial and angular correlations are crucial in doubly-excited states (Ho & Callaway 1984, 1986; Pathak *et al.* 1988). The higher the excitation and, therefore, the further removed are the electrons from the central attraction and the slower they get, the more important these correlations become, reaching an extreme near the 14.35 eV energy of the threshold for double break-up. Increasingly, independent particle pictures lose their meaning as each electron feels as much of a force from the other as it does from the

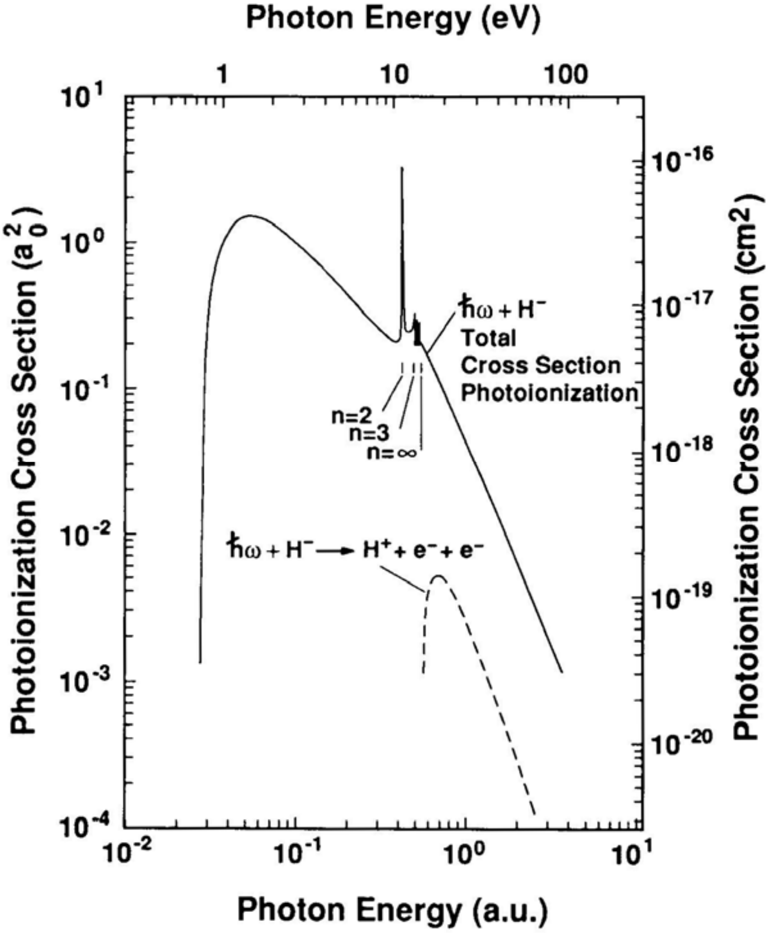

Figure 6. Extension of photodetachment cross-section of H^- in fig. 2 to higher energies, with horizontal axis reversed, photon energy now increasing to the right, and showing doubly-excited states as sharp resonances (from Broad and Reinhardt 1976).

nucleus and proper understanding requires a treatment of the three-particle system as a whole with a joint description of both electrons – a “pair” of electrons. Pair quantum numbers and even pair coordinates are, therefore, part of the story of H^- in the 10 –16 eV energy range (Rau 1984b).

Angular: A glance at fig. 5(a) suffices to emphasize that strong angular correlations set in already at N = 2 with the first doubly-excited states. This is because states differing only in *l*, such as $2s^2$ and $2p^2$, or *2sns* and *2pnp*, are degenerate in the absence of the electron-electron interaction and, therefore, will be strongly mixed when that interaction is taken into account. Put another way, in the presence of the electric field due to the other electron, the degenerate *1* states of the hydrogenic manifold of one electron are strongly mixed so that *1* loses meaning as a quantum number. A first step is to use degenerate perturbation theory within the set of $(nl)^2$

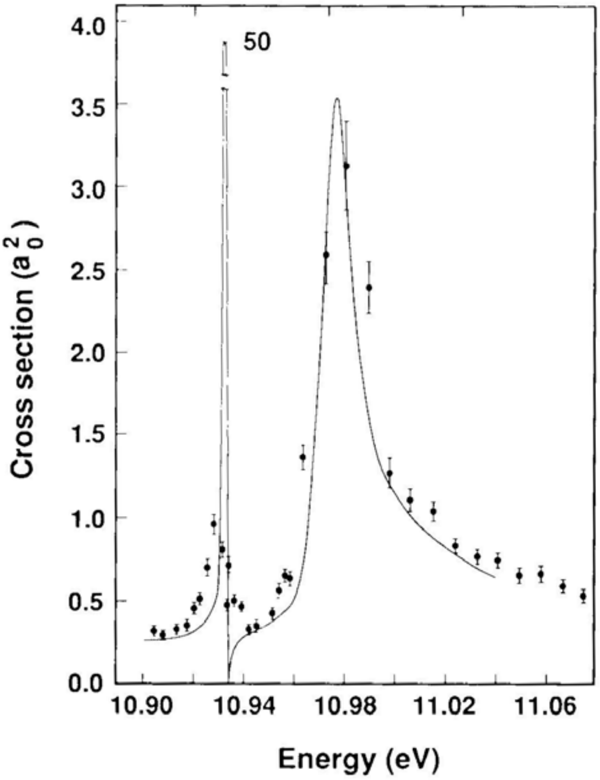

Figure 7. Doubly-excited $^1P^\circ$ resonances of H^- in the vicinity of the H(N = 2) threshold as observed in the photodetachment cross-section, with a sharp "Feshbach" resonance just below and a broad "shape" resonance just above the 10.95 eV threshold (from Bryant *et al.* 1977).

states (for ^1S symmetry, and counterparts for other values of L, S and J) to get new eigenstates that include the $1/r_{12}$ interaction. The label l is thereby replaced by $v = 0,1,2,\ldots, (n-1)$, which is the first of such "pair quantum numbers" and which may be regarded as the quantum number associated with θ_{12}, the angle between $\hat{r}_1$ and $\hat{r}_2$.

The mixing coefficients in $|v\rangle = \sum_l \langle l/v|\rangle l\rangle$ can be obtained by numerical diagonalization (Rau & Molina 1989; Rau 1990a,b) and are seen to be very well described by analytical expressions from a group-theoretical model (see a review: Herrick 1983). In this description, the product of the individual SO(4) representations that hold for each electron independently (the well-known symmetry of the hydrogen atom) is reduced to a single SO(4) for the pair to provide simple analytical formulae for $\langle l|v\rangle$. Examination of the corresponding wave functions of the mixed states $|v\rangle$ shows, as may be expected, that the lowest-lying state with $v = 0$ has a concentration at $\theta_{12} \simeq \pi$ which minimizes the electron-electron repulsion whereas the state at the opposite end with $v = n-1$ has a concentration around $\theta_{12} = 0$. The former

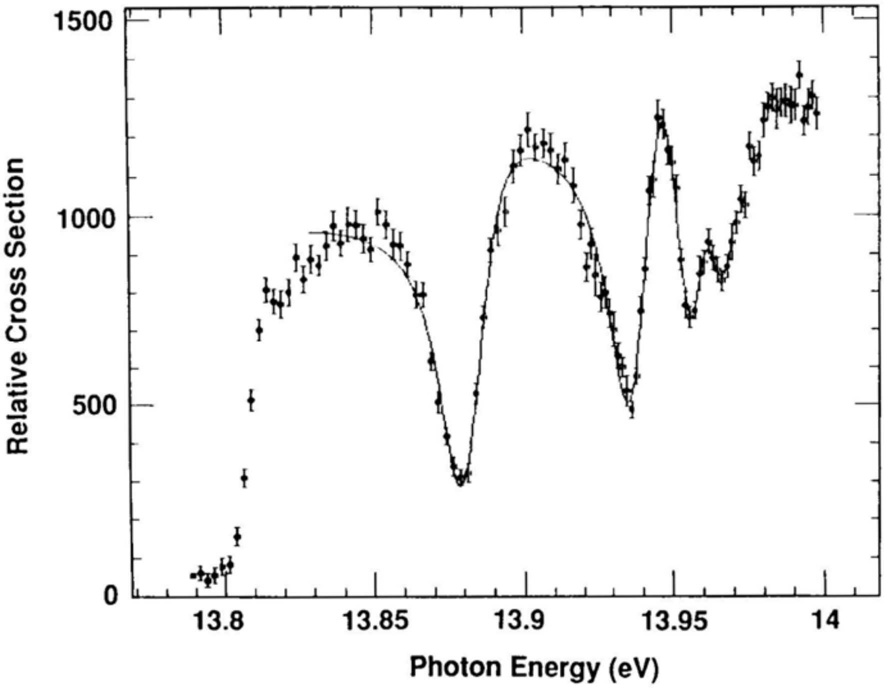

Figure 8. $1P^\circ$ resonances of H^-below the H(N = 5) threshold, with data fitted to "Fano resonance profiles" (from Harris *etal.* 1990).

is of greatest interest because it describes the lowest energy states with greatest stability. The concentration at $\theta_{12} \simeq \pi$ in this state is seen to have a width that scales as $n^{-1/2}$. The extreme concentration due to angular correlation, reached as $\eta \to \infty$, the double-detachment threshold, has the two electrons lying on opposite sides of the nucleus (Rau 1990a). The SO(4) model also applies to $L \neq 0$ states in which the individual l_1 and l_2 values of the electrons need not be equal, leading to two pair quantum numbers, called *K* and *T*, which replace l_1 and l_2 (Herrick 1983). The former, simply related to *v*, is associated with the pair coordinate θ_{12}, whereas *T* is a measure of $(L \cdot \hat{r}_<)^2$, that is, of the projection of the total orbital angular momentum on the radial vector of the inner (N) electron (see, for instance, sections 10.3 & 10.5.2 of Fano & Rau 1986).

Radial: Whereas angular correlations are similar in all doubly-excited states, having their origin in the degenerate *l*-mixing, under radial correlations two-electron excitations divide into two classes. One, with an "in-out" aspect as in section 2.3 for the ground state of H, has $r_> >> r_<$, whereas the second group has comparable radial excitation ($r_1 \simeq r_2$) of the two electrons. The first group may be termed "planetary" (Percival 1977) in that each electron can be ascribed an individual principal quantum number (or orbit) with n > N, these one-electron quantum numbers retaining their meaning (Rau 1984b). Such states in H^- may also be termed “Coulomb-dipole” because the inner electron sees a dominant Coulomb field whereas the outer electron sees the dipole field of the other two particles (this is again the permanent electric dipole moment or the “linear Stark effect” of H($N \geq 2$) arising from the degenerate *l*-mixing). In He and other isoelectronic analogs, however, such planetary states have both electrons seeing a Coulomb attraction, the outer having in addition a dipole field. The second class of states with a radial correlation such that both electrons share comparably the excitation energy have been called “Wannier ridge” states (Buckman *et al.* 1983) and for them H^- and He are essentially similar. In their description, particularly as one approaches the double-detachment threshold, a true pair picture with no reference to independent particle coordinates (r_1 and r_2) or quantum numbers (N and n) or ionization limits (N) becomes necessary (Rau 1983 & 1984b).

4.3 *Hyperspherical coordinates and two-electron Schrödinger equation*

Over the last twenty-five years, the study of doubly-excited states has prompted the use of a set of coordinates that deal with the pair of electrons from the start (cf. chapter 10 of Fano & Rau 1986; Lin 1986). An alternative, which also treats the three-body system as a whole, sets up a correspondence between H^- and H_2^+, using the language of molecular orbitals and potential wells, r_{12} playing the role of the internuclear distance R (Feagin & Briggs 1986, 1988; Rost & Briggs 1988; Feagin 1988). Both these approaches have common elements and have been useful in understanding doubly-excited states. I will now turn to the more direct recasting of $\vec{r}_1$ and $\vec{r}_2$ of the atomic system in terms of joint coordinates called hyperspherical coordinates, because this also generalizes immediately to problems involving more electrons. These coordinates were actually first introduced by Bartlett (1937) and Fock (1954) in the study of the ground state of He, to handle the description of the wave function wherein both r_1 and r_2 go to zero, the same considerations applying also of course to H^-. The coordinates were also invoked by Wannier (1953) over forty years ago in treating the threshold double escape of two electrons (we will return to this in section 5) before they were popularized in recent years for the study of doubly-excited states.

The angle θ_{12} between $\hat{r}_1$ and $\hat{r}_2$ has already been introduced. Next, the radial distances are replaced by the “circular coordinates” in the r_1 —r_2 plane, $R = (r_1^2 + r_2^2)^{1/2}$, $\alpha = \arctan(r_2/r_1)$ Together with the three Euler angles to describe the position of the (proton + electron + electron) plane in space, the coordinates R, α, and θ_{12} provide a set of six “pair coordinates” to replace ($\vec{r}_1$, $\vec{r}_2$) in the independent-particle picture. The three pair coordinates also provide a very natural description of the system, with R providing the overall size and a measure of excitation, α indexing the radial correlation, and θ_{12} the angular correlation between the electrons. For a general three or N > 3-body system with arbitrary masses for the particles, hyperspherical coordinates can be defined to incorporate the masses so that $R \equiv [\sum_i m_i r_i^2 / \sum m_i]^{1/2}$ is actually the radius of gyration (Fano 1981).

The coordinates then are those of a 3(N – l)dimensional sphere with R the radius and $\hat{R}$ the hypersurface of such a sphere.

The Schrödinger equation for H^- or its isoelectronic analogs takes the following form in hyperspherical coordinates and in atomic units (cf. section 10.4 of Fano & Rau 1986):

$$\left[-\frac{1}{2}\left\{\frac{d^2}{dR^2}-\frac{\Lambda_{\hat{R}}^2+15/4}{R^2}\right\}+\frac{Z(\hat{R})}{R}\right] R^{5/2}\, \Psi\,(\vec{R}) = ER^{5/2}\, \Psi\,(\vec{R}), \tag{4}$$

where Λ_R^2 is the Laplacian or "grand angular momentum" operator involving derivatives with respect to α and θ_{12} (the counterpart of L^2 in three dimensions), and $Z(\hat{R})$ is an "effective charge operator":

$$Z(\hat{R}) = -Z\left(\frac{1}{\cos\alpha}+\frac{1}{\sin\alpha}\right)+\frac{1}{(1-\sin 2\alpha\cos\theta_{12})^{1/2}}. \tag{5}$$

Each of the three terms in (5) arises from the three pairs of Coulomb interactions in the system once a common dimensional 1/ R element has been factored out. The "potential surface" described by $Z(R)$ in (5) is shown in fig. 9. Note deep valleys at $\alpha = 0$ and $\pi/2$ which correspond to r_2 or r_1 vanishing and an infinite repulsion at $\alpha = \pi/4$, $\theta_{12} = 0$ which marks the electron-electron repulsive singularity at $\vec{r}_1 = \vec{r}_2$. Only half the potential surface from $\theta_{12} = 0$ to π is shown, the identity of the two electrons repeating a reflected segment of fig. 9 for $\theta_{12} = \pi$ to 2π. Finally, the surface has another critical point, a saddle at $\alpha = \pi/4$, $\theta_{12} = \pi$, that is, when $\vec{r}_1 = -\vec{r}_2$. This saddle point will be crucial in the rest of this story.

The H^- -Schrödinger equation in hyperspherical coordinates takes the form in (4) which is very similar to that of hydrogen in three-dimensional spherical coordinates, with a radial and angular kinetic energy and a Coulomb potential. The major difference is that the charge depends on the hyperangles, making the equation non-separable. Since other multi-particle problems of atomic and molecular systems also take a form similar to (4) with 3(N – 1) -dimensional hyperspherical coordinates (and 5/2 replaced by (3N – 4)/2) and a charge that depends on the (3N – 7) hyperangles, the H^- system takes on added significance as a prototype for such non-separable problems. In particular, the potential surface in fig. 9 is the simplest prototype of such multi-dimensional potential surfaces, so that the understanding of quantum-mechanical solutions of a configuration point moving on such a surface may be expected to play the same role in shaping our intuition about more general problems of chemical transformation as the Coulomb and harmonic oscillator potentials have played for two-body problems in physics. Besides maxima and minima, there is one saddle point in such a two-variable potential surface which will turn out to be especially interesting for the rest of our story of H^- and also of especial significance generally because saddle points proliferate when more variables are involved.

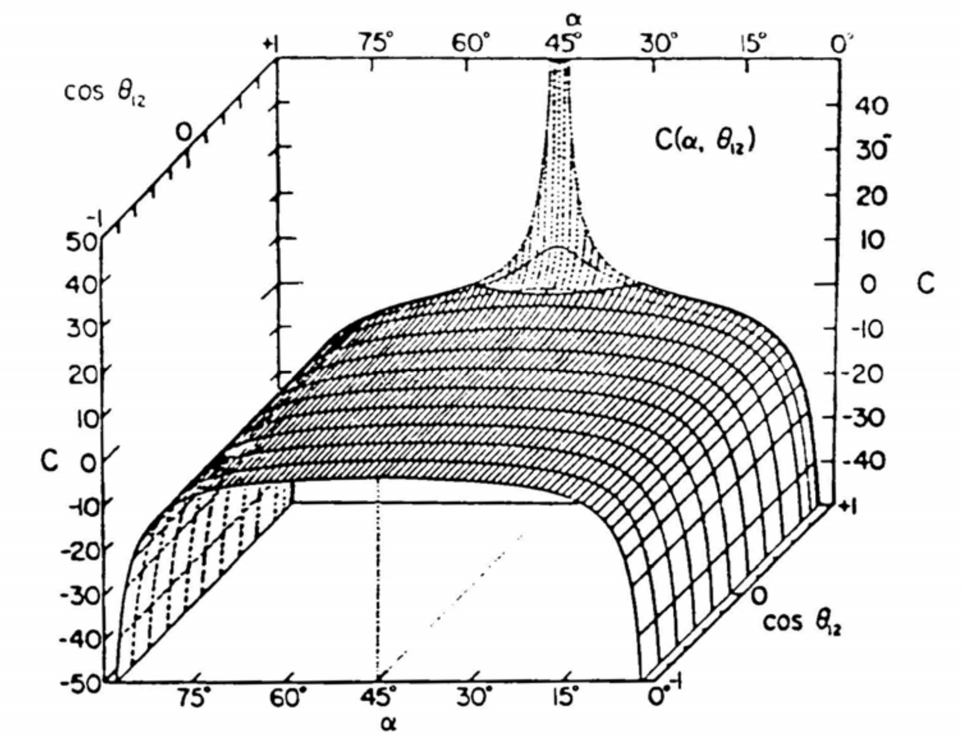

Figure 9. Potential surface $C(\alpha, \theta_{12}) = Z(\hat{R})$ in (5) for H^- in hyperspherical coordinates (from Lin 1974). Note valleys at $\alpha = 0$ and $\pi/2$, a peak at $\alpha = \pi/4$, $\theta_{12} = 0$, and a saddle point at $\alpha = \pi/4$, $\theta = \pi$.

4.4 *Low-lying states — adiabatic treatment*

The Schrödinger equation in (4) is non-separable so that no exact solutions are feasible. The different scaling in R of the Coulomb potential and angular kinetic energy, together with the dependence of Z on $\hat{R}$ are at the heart of this non-separability, so that expansion/excitation of the system (in R) is inextricably coupled to the radial and angular correlations (in α and θ_{12}, respectively). For the low-lying doubly-excited states, however, that is, with $N \leq 6$ in fig. 5, an adiabatic separation of R from α and θ_{12} has proved successful (Macek 1968). That is, correlations develop faster than the general expansion of the system under excitation. Much as in the Bohr-Oppenheimer procedure for molecules, with R held fixed, the angular part of the Hamiltonian is solved to provide R-dependent eigenvalues and eigenfunctions,

$$\left[\frac{1}{2}\Lambda_{\hat{R}}^2 + RZ(\hat{R})\right] \Phi_\mu (R; \hat{R}) = R^2 U_\mu(R) \Phi_\mu (R; \hat{R}). \tag{6}$$

These so-called “channel functions” then provide a basis for expansion of the wave function Ψ in (4):

$$\Psi(\vec{R}) = \sum_{\mu} F_{\mu}(R)\ \Phi_{\mu}(R;\hat{R}). \tag{7}$$

The eigenvalues U_{μ} (R)appeal as potential wells in the resulting coupled radial equations for $F_{\mu}(R)$, the coupling between μ and μ' provided by matrix elements of d/dR and d_2 $/d$ R^2 between Φ_{μ} and $\Phi_{\mu'}$. The initial adiabatic approximation neglects these couplings, viewing each $F_{\mu}(R)$ as an eigenfunction of a single potential well U_{μ} (R),the resulting eigenvalues being the doubly-excited state energy levels (Lin 1986; chapter 10 of Fano & Rau 1986).

A variety of different approaches may be used to solve (6) to get the U_{μ} and Φ_{μ}. One is to expand Φ_{μ} in terms of the basis provided by the “hyperspherical harmonics” that are the eigenfunctions of Λ_R^2 and are analogs of the ordinary spherical harmonics (Vilenkin 1968; Avery 1988). Generally, the adiabatic hyperspherical calculations have viewed doubly-excited states as groups converging to H(N) plus electron and, therefore, at large R have imposed the corresponding boundary conditions in defining the channel functions. Fig. 10 shows the three lowest potential curves in the vicinity of the N = 2 threshold (Lin 1975, 1976). In independent particle terms, 2 *snp* and 2 *pns* states are strongly mixed in the combinations marked + and –, together with a smaller admixture of the third configuration, 2*pnd,* of this $^1P^{\circ}$ symmetry (Cooper *et al.* 1963). The curve marked – has a long range attractive tail which corresponds to the $1/r^2$ dipole potential on the outer electron because of the 2*s* – 2*p* degeneracy of H(N = 2). This well holds an infinite number of “dipole-bound” states, the lowest of which is in very good correspondence with the experimentally observed sharp feature, a “Feshbach resonance”, in fig. 7. The other broader feature in that figure is seen to correspond to the + curve in fig. 10 which has a broad barrier region for $R > 15a_0$, a state just above the – 0.25 a.u. N=2 threshold energy being temporarily trapped by this barrier to appear as a “shape resonance”. For a molecular orbital treatment and labeling of similar potentials to those in fig. 10, see Feagin (1988).

Adiabatic hyperspherical calculations have been carried out to higher N, the most extensive H^- study in Koyama *et al.* (1989); Sadeghpour & Greene (1990) and Sadeghpour (1991). Fig. 11 shows a sequence of potential wells and of doubly-excited state Feshbach resonances held in the lowest well which has an asymptotic attractive potential due to the dipole moment of H(N). These resonances conform well (Sadeghpour 1991) to the experimental data, as illustrated in fig. 8. In each of these Rydberg series below each H(N) threshold, the lowest level N = n in independent particle language) fits a “six-dimensional Rydberg formula” (Rau 1983) to be discussed further in section 5, while higher members of the series (with n > N) then fit the spacings expected of “dipole-bound” states (Gailitis & Damburg 1963; Gailitis 1980). The greatest numerical accuracy at lower N has been achieved by a so-called “diabatic-by-sector” handling of the coupled hyperspherical equations (Tang *et al.* 1992).

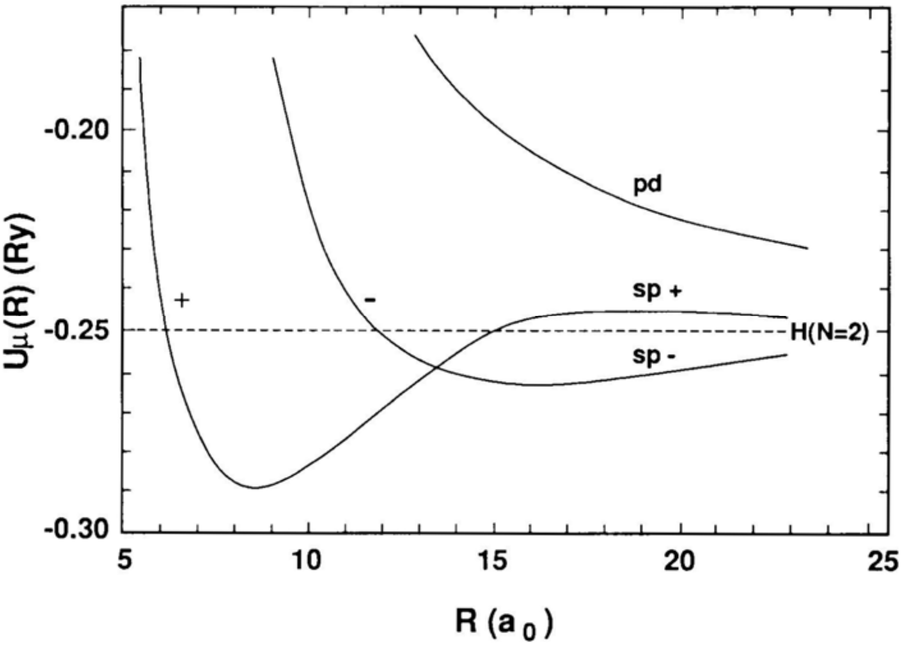

Figure 10 Adiabatic potential wells $U_\mu(R)$ in (6) for $^1P^o$. States of H^- converging to H (N=2) (From Lin 1975).

4.5 *Doubly-excited states in an external field*

The same Los Alamos experiment that observed the doubly-excited states of H^- shown in figures 6–8 has also studied the effect of a strong electric field on them (Gram *et al.* 1978; Bryant *et al.* 1983). Of the two N = 2^1 P^o resonances in fig. 7, the sharp Feshbach one was seen to show a linear Stark effect due to mixing with an almost degenerate ^{1} S^e resonance (Callaway & Rau 1978; Wendoloski & Reinhardt 1978). With increasing strength of the external electric field, the resonance finally disappears, whereas the shape resonance just above threshold persists to even larger fields. Hyperspherical calculations that give the potential barrier in fig. 10 which accounts for this resonance have been extended to include the effect of the electric field on this barrier and, thereby, on the resonance (Lin 1983; Slonim & Greene 1991; Du *et al.* 1993). Similar studies have also been carried out for N = 4 and 5 (Zhou & Lin 1992), and also by conventional configuration interaction calculations with independent particle functions (Ho 1995; Bachau & Martin 1996).

Of particular interest among the N = 2 states is the lowest one of $^3P^e$ symmetry, described in independent-electron terms as $2p^2$. This is bound below the H(N = 2) threshold with about 9.6 meV. The only one-electron continuum at this energy being H(N= 1)+ electron which cannot form a state with quantum numbers $^3P^e$, this state is forbidden to autoionize. It can only decay into this continuum by also simultaneously radiating a photon along with the electron, these two particles sharing the excess energy of ≃ 10.2 eV (Drake 1973). The inverse process of

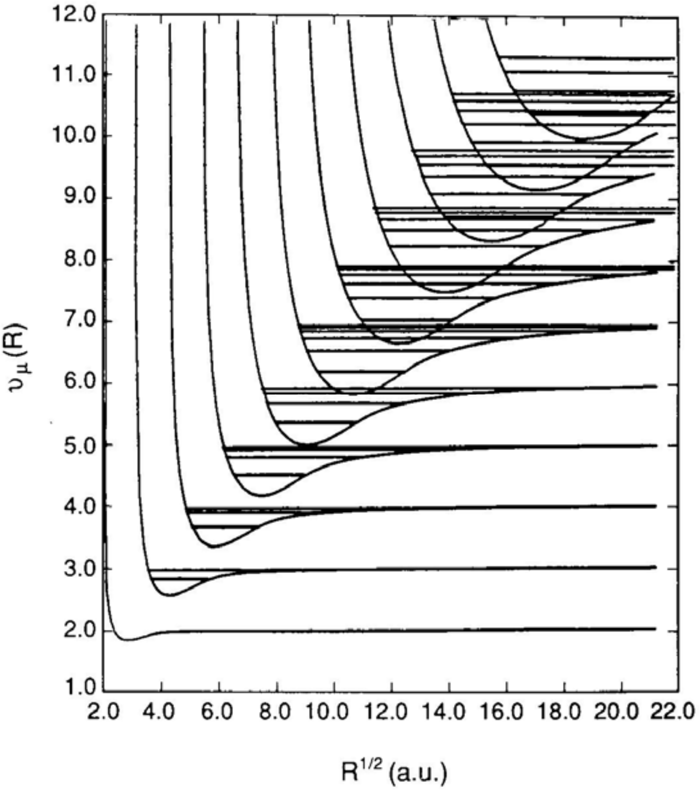

Figure 11. Similar to fig. 10 but showing only the lowest potential well for $^1P^o$ states below successive thresholds H(N). Plotted are effective quantum numbers $\nu_\mu\ (R) = [-U\mu(R)/\ 13.6\ \mathrm{e\ V}]^{1/2}$ as a function of $R^{1/2}$. in each well, the lowest bound states are shown as horizontal lines (from Sadeghpour & Greene 1990).

radiative attachment, H(N= l)+e + $\gamma \rightarrow +$ H ($^3P\ ^e$) has been suggested as an efficient absorption mechanism for ultraviolet light (Drake 1974) and has been observed in rocket measurements of Zeta Tauri stars (Heap & Stecher 1974). This very long-lived H^- state has not so far been observed in the laboratory but double detachment (Mercouris & Nicolaides 1993) and photodetachment to the 2*s*2*p* $^3P°$ state (Du *et al.* 1994) have been studied theoretically as possibly feasible experiments.

5. High excitation and the double continuum

As discussed in the previous section, we have now a fairly good and complete understanding of the low-lying doubly-excited states of H^-, both experimentally and theoretically, including the nature of radial and angular correlations in them. For states above N = 6, however, and as the double-detachment threshold at 14.35 eVis reached, our knowledge is extremely fragmentary (Nicolaides & Komninos 1987;

Pathak *et al.* 1989; Ho 1990, 1992). Experimental data on the series converging to such larger values of N are sparse and show, as also in He in the corresponding energy range, $\simeq$ 79 eV (Domke *et al.* 1991, 1995; Wintgen & Delande 1993), that the series overlap and perturb one another. Hyperspherical treatments as in fig. 11 lead to the same conclusion of many overlapping potential wells (Sadeghpour 1991). Although at first some analysis can and has been carried out to handle interlopers perturbatively, it is clear that this cannot extend to really high N and the double-detachment threshold. This is due to the very nature of a Coulomb potential with its high density of states. In the similar situation of one electron in a three-dimensional Coulomb potential (plus shorter range distortions), quantum defect theory, based on continuity properties in the vicinity of the ionization threshold, affords effective handling of a highly excited electron (chapter 5 of Fano & Rau 1986). Now, for a pair moving in the six-dimensional Coulomb field in (4), it is likewise natural to focus on the double-detachment threshold as the starting point on which to base analysis of the higher reaches of the doubly-excited state spectrum (Rau 1984b).

5.1 *Description as a pair of electrons*

The methods described in sections 4.3 and 4.4 while employing joint or pair coordinates, nevertheless, do not give up completely the crutch of independent-particle descriptions. In particular, the use of N, the inner electron's principal quantum number, both in the classification of doubly-excited states and in developing the channel functions $\Phi\mu$ to converge to successive single-detachment thresholds, introduces an element foreign to a fully pair treatment. Indeed, calculations revert at large R even to the independent-particle coordinates r_1 and r_2 to get efficient convergence to the single-detachment thresholds (Christensen-Dalsgaard 1984). Only recently have treatments emerged that depart from this, proceeding to large R without ever reverting to single particle aspects (Zhang & Rau 1992; Heim *et al.* 1996). Once double detachment is energetically possible above 14.35 eV, it is also *the pair* that escapes to $R = \infty$ as emphasized in Wannier's treatment of the threshold law for this process, a point of view essentially different from all others that regard *two electrons* as escaping from a central positive charge (Rau 1971, 1984 b,c).

The focus on the pair coordinates (R, α, θ_{12}) throughout also organizes the spectrum of doubly-excited states in fig. 5, the quantum numbers μ, and the potential wells, in an alternative but very different way from the discussion so far. Thus, instead of series associated with each N as in fig. 5(a), consider the alternative in fig. 5(b) where the same levels have been redrawn with no reference to N and grouped differently (Rau 1984b). For each v, the pair quantum number that indexes the number of nodes in θ_{12}, levels drawn similarly (solid, dashed, etc., lines) form series converging to the double-detachment threshold. For the system of a pair of electrons in a Coulomb field, this is the only limit compatible with the picture of the system as a whole, shorn of all independent-particle aspects (Read 1982; Rau 1983, 1984b). A pair principal quantum number v, conjugate to R, and a "radial correlation quantum number" η, which counts the nodes in α, provide an alternative basis $| \ \nu, \eta, \upsilon\rangle$ to the adiabatic hyperspherical basis, $|\mathrm{N}, n, \nu,\rangle$ or the independent-particle basis, $|\mathrm{N}, n\ , l\rangle$ The H^- Schrödinger equation does not separate in any coordinate system and, as in any such non-separable problem, any complete basis set affords a description of the whole system. The choice among alternatives is made on the basis of appropriateness, one or the other affording a more economical description depending on the energy range. For the high doubly-excited states and nearby double continuum in the vicinity of 14.35 eV, when many basis states of the other sets are strongly mixed, it is the $|\nu, \eta, \nu\rangle$ that more nearly conform to the physical eigenstates.

States with the same ν and η but successive values of ν form a "six-dimensional" Rydberg series with an appropriate Rydberg formula (Rau 1983) and, as already noted in section 4.4, provide a good description of the lowest states below each N. Examination of their wave functions is also instructive. The adiabatic hyperspherical calculations such as in fig. 11 had already noted (Lin 1986) that the channel functions Φ_μ near $R = R_{min}$ for the lowest potential well converging to each N showed a concentration of the wave function near $\alpha = \pi/4$, $\theta_{12} = \pi$, the configuration in which the two electrons are on opposite sides of the nucleus at equal distances and which is the saddle point of fig. 9. Viewed as a set of potential wells, this concentration passed at larger R from one well to the next of higher N roughly in the vicinity of the prominent avoided crossings seen in fig. 11. The locus of avoided crossings in such a figure is well described by the value of the potential at the saddle point, namely, $Z(\hat{R} = \text{saddle point})/R$.

This suggests an alternative "diabatic" handling of the hyperspherical Schrödinger equation in (4), wherein the set of lowest wells of fig. 11 is replaced by the single well in fig. 12 that tracks at large R essentially the saddle value and converges to the double-detachment threshold (Heim & Rau 1996). At small R, this potential coincides with the lowest well, that is, to the lowest eigenvalue λ of the Λ^2 angular momentum operator which dominates at small distances. The lowest states in each of the wells in fig. 11 are thereby seen as a single sequence in the single potential well of fig. 12. Although the energy positions are little changed, there is a drastically different picture of the wave functions in the two pictures. In fig. 11, each state has a radial wave function that is nodeless in R, the higher ones having more nodes in the hyperangles (while, at the same time, all having peak probability density at the saddle point). Instead, all the states in fig. 12 have no nodes in angles, having traded them for successive nodes in R (see also Bohn 1994 and Bohn & Fano 1996). The two pictures are drastically different for a matrix element such as the one involved in photoabsorption from the ground state. Because of the staggering in R of successsive wells in fig. 11, the wave functions at higher N are very (exponentially) small at small R which is where the ground state function is concentrated. Therefore, the matrix element and cross-section for photoabsorption decreases exponentially in N on comparing excitation of this set of states. In fig. 12, on the other hand, the successive states ν have more nodes in R and the oscillating loops of the wave function at small R have more overlap with the ground state, the photoabsorption cross-section dropping off thereby as a power of ν just as is indeed observed. Once

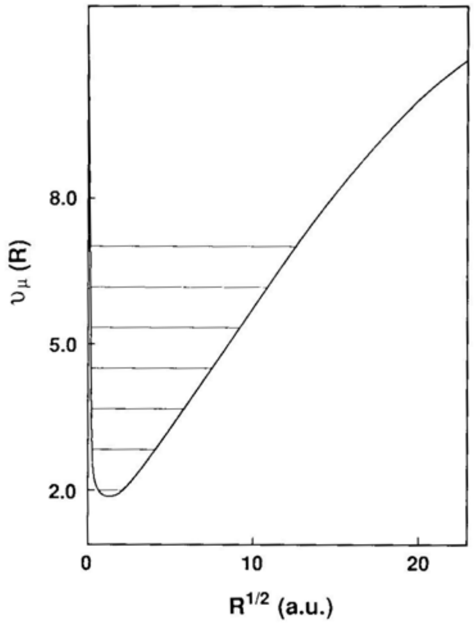

Figure 12. Lowest (η = 0) diabatic potential well for pair states, corresponding to the set in fig 11. At small *R*, it coincides with the lowest of that set while, at large *R*, it traces through the loci of avoided crossings to converge to the double-detachment threshold.

again, note the one-electron analogy, the description in fig. 11 being like a sequence 2*p*, 3d, 4*f*, ..., all nodeless in *r* but with more angular nodes, whereas fig. 12 is more like 2*p*, 3*p*, 4*p*, ..., that is, with the same angular structure but more radial nodes. Energy considerations alone do not suffice for characterization in a Coulomb problem, given the high degeneracy. One has to examine wave functions as well and, clearly, the second picture is more in conformity with the excitation of a Rydberg series, now of double excitations (Heim *et al.* 1996; Heim & Rau 1996).

5.2 *Threshold escape of the pair*

A sequence such as in fig. 12 of doubly-excited states connects as $\nu \to \infty$ to the double continuum above the 14.35 eV threshold. The threshold behaviour of double escape is, therefore a natural adjunct to the study of highly-excited states (Rau 1971, 1984b). For a one-electron Coulomb problem, the feature that the photoabsorption cross-section to successive *n* falls off as n^{-3} connects to the finite and constant photoionization cross-section just above threshold (section 2.5 of Fano & Rau 1986). For the two-electron problem, the threshold law was studied by Wannier (1953) long before any doubly-excited states had been observed. He recognized that the correlations between the electrons are at an extreme at threshold given that the electrons are slow, allowing for a long range over which their motion can remain correlated. A joint, pair treatment was therefore essential and he described one based on classical mechanics. With reference to our discussion and in the language of quantum physics, the final state of double escape has to be handled correctly in terms of the pair's escape to infinity (Rau 1971, 1984c).

It is the final state wave function at large distances that governs the threshold law and this has to be obtained from (4) for $E \geq 0$. The kind of radial and angular correlations that prevail in the so-called "ridge" states described in section 5.1, with wave function concentration in the saddle of the potential surface, also pertain to the threshold wave function. Unless the two electrons maintain an equal sharing of the available energy for most of the escape (that is, stay in the vicinity of $\alpha = \pi/4$), double escape will be thwarted, one or the other getting faster at the expense of the other which will then fall back into a bound state H(N). This instability towards falling away from the saddle into the valleys at $\alpha = 0$ and $\pi/2$ in fig. 9 acts as a suppression mechanism (Rau 1971). In its absence, the escape of two electrons described as a product of two Coulomb wave functions, would give a threshold cross-section proportional to E. A "Coulomb-dipole" description (Temkin & Hahn 1974; Temkin 1982), with a Coulomb wave for the inner and a dipole wave for the outer electron, would give a similar result (Greene & Rau 1985). The additional suppression in the Wannier pair description raises the exponent from 1; since the saddle potential and departures from it involve Z, so does this exponent. Both Wannier's analysis and a pair hyperspherical treatment of the quantum problem (cf. a review: Rau 1984c) give the value 1.127 for this exponent for $Z= 1$ which applies both to photo double-detachment of H (photon energy = 14.35 + E) and electron-impact ionization of H (incident electron energy = 13.6 + E).

Once again, only the Los Alamos experiment, with its relativistic Doppler amplification of laser photon energies to about 15 eV, has been able so far to study the double detachment. Fig. 13 shows a crosssection that is indeed compatible with the E threshold law (Donahue *et al.* 1982). Other details of the outgoing electrons, such as the distribution in the mutual angle θ_{12}, or the angular distribution of one electron with respect to the laser polarization, or spin correlations between the electrons have not been measured. Theoretical predictions exist on all these (Rau 1984c, 1990a; Kato & Watanabe 1995) but the relativistic velocity of the H^- beam makes the electrons emerge in a very forward direction as seen in the laboratory, making their experimental observation difficult. Such measurements will have to await laboratory photodetachment studies once tunable lasers are available in the 15 eV energy range.

The double continuum of H^- can also be studied in electron-impact ionization of hydrogen. Again, unlike similar studies of threshold ionization of He and other rare gases by electrons, no such measurements have been made except for one on the spin dependence of this ionization. The asymmetry parameter for triplet and singlet double-detachment has been studied close to threshold and compared with theoretical predictions (Guo *et al.* 1990, Crowe *et al.* 1990, Friedman *et al.* 1992).

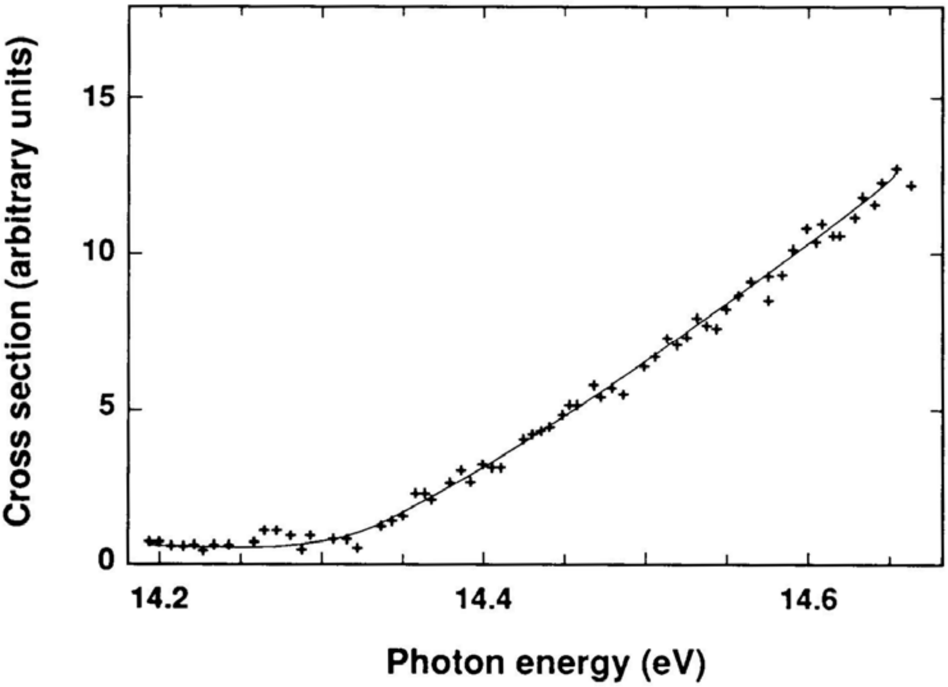

Figure 13. Cross-section for photo double-detachment of H⁻ just above the 14.35 eV threshold (from Donahue *et al.* 1982).

6. Collisions with other particles

We have discussed so far the structure of H^- and its interactions with the electromagnetic field. Collisions involving H^- and a second particle have also been studied (see reviews by Risley 1980, 1983; Esaulov 1986). One, already noted at the end of section 2.3, is collision with H^+, leading to charge exchange or associative attachment to form H_2^+, processes of interest in stellar atmospheres. Collisions of 1–25 keV H^- ions with Na have also been studied (Allen *et al.* 1988), as well as with noble gases and small molecules over a range of energies from about 100 eV to a few ten keV (Tuan & Esaulov 1982; Montmagnon *et al.* 1983; Andersen *et al.* 1984). In the case of molecules, charge exchange to shape resonances plays a major role. Below about 1 keV, an adiabatic molecular picture based on the zero-range model of H^- gives an adequate description whereas at higher energies an impulse approximation for the scattering of the loose electron suffices. There are also theoretical predictions of novel structures in H^- collisions with atoms (Theodosiou 1991).

Collisions with electrons, also likely in astrophysical contexts, have been studied in the laboratory, particularly with the advent of cooled storage rings for ions. An H^- beam in such a ring is merged with an almost parallel electron beam so that a low energy process such as detachment, $e + H^- \rightarrow H + e + e$, can be studied. This time, unlike in section 5, the double escape is not in a Coulomb but in an asymptotically *neutral field. Careful measurements (Andersen et al.* 1995) show no resonances of states of H^{--} but, were metastable resonance states to exist (Lieb 1984 and Simon 1974 have proven thát no stable bound states exist and experimental searches (Chang *et al.* 1987) have also been negative), they might be of importance in astrophysics. In analogy with the tightly correlated Wannier state of two electrons, a similar state of three low energy electrons in a Coulomb potential would be in the saddle point of the potential surface and have the geometrical configuration of an equilateral triangle, the electrons at the vertices and equidistant form the nucleus at the center Such a tight correlation, with $r_1 = r_2 = r_3$, and the mutual angles between the $\hat{r}_i$ equal to $2\pi/3$, would only result from a superposition of a very large number of angular harmonics, which might account for why it has escaped notice in theoretical calculations so far (Robicheaux *et al.* 1994).

Finally, the latest experiments from Los Alamos are worth noting, in which the relativistic H^- beam is passed through thin carbon foils (Mohagheghi *et al.* 1991). The time of interaction is less than a femtosecond, the H^- experiencing a pulse of the "matter field". Remarkably, many H^- ions emerge unscathed, although both neutral H and protons H^+ a re also observed. The distribution in principal quantum number of the neutrals has been studied, showing a falloff roughly proportional to n^{-3} for low n ($n = 2$–5) but a much steeper n^{-8} for higher n (10 – 15). Our understanding of these results and of the interaction of the negative ion with the foil is as yet very incomplete.

7. Epilogue

The H^- ion has played an important and central role from the earliest days of quantum physics. As the simplest, and therefore prototype, threebody quantum system with long range interactions between all pairs of particles, its relevance extends beyond atomic physics to multiparticle problems of chemical transformation and even more general physics. All three regions of energy, the ground state and photoab sorption continuum for visible and near ultraviolet, the low-lying doubly excited states into the "middle ultraviolet" ($\simeq$ 10 – 13 eV), and the high doubly-excited states and double continuum in the "far ultraviolet" (> 14 eV), exhibit interesting and different effects of electron-electron correlations in this system. This essay has discussed the nature of these correlations and the associated structures, based on the understanding gained from laboratory experiments and theoretical studies over the years. Applications, some central as described by Chandrasekhar over fifty years ago, to astrophysics, and the use of H^- as the initial species for acceleration in particle physics accelerators and plasma machines, add further interest to this fascinating species. New techniques that are just emerging, such as the advent of far ultraviolet telescopes, detailed coincidence measurements of energy, angular and spin distributions of two electrons, stored beams of H^- which can be intercepted by other particles over a wide range of collision energies, etc., are likely to give even further insight into the physics of H^- and add to the applications in varied areas of physics and astrophysics.

I had just begun the writing of this essay when my close friend and colleague, the astrophysicist Ganesar Chanmugam, passed away unexpectedly. In our long association, we had many discussions, including some on H^- and its early history. These many memories have been very much in my mind as I wrote and I wish, therefore, to dedicate this first paper after his death to him and to his many contributions.

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