Dominant Photodetachment Channels in H^-

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Adiabatic hyperspherical potential curves are calculated for very highly excited states of H^- converging to $H(n \leq 12)$. These potential curves reveal surprisingly weak channel interactions, manifested as extremely diabatic multiple curve crossings. We demonstrate that only resonances associated with the *lowest* "+" diabatic channel within each n manifold are observed in the recent experiments at Los Alamos (Harris *et al.*). A simple Rydberg-dipole formula gives the positions of all dominant resonances, permitting extrapolation to arbitrarily high quantum numbers.

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Our understanding of electron-electron correlation effects in doubly excited states has advanced on several fronts since the first observations of doubly excited lines in the photoionization spectrum of He in the early 1960's.[1-6] Among these theoretical methods, Macek's[6] adiabatic hyperspherical coordinate treatment has accounted for many of the systematic properties of doubly excited states, while providing qualitative insight into the delicate balance between the electron-nucleus attraction and the electron-electron repulsion in doubly excited levels. This representation exploits the natural symmetry of any two-electron atom by introducing a collective coordinate system: a hyperradius $R=[r_1^2+r_2^2]^{1/2}$, giving a measure of the "size" of the complex, and a hyperangle $\alpha=\arctan(r_2/r_1)$, defining the degree of radial correlation between two "valence" electrons. In Macek's adiabatic approach,[6-8] the two-electron Hamiltonian is diagonalized parametrically in R,

$$\hat{U}(R;\Omega)\Phi_\mu(R,\Omega)=U_\mu(R)\Phi_\mu(R,\Omega)\,, \qquad (1)$$

and the eigenvalues serve as potential-energy channels for motion of the electron pair. All doubly excited resonant states in any one particular hyperspherical channel will exhibit the same correlation signature.[7]

Approximate correlation quantum numbers (the so called $A\equiv$ "+" and "−," and KT)[2,7] have been used to classify the hyperspherical channels and establish the dominance of the + channels over the − channels. The purpose of this paper is however to report on a new selection rule in the photodetachment process of H^-, establishing the dominance of a few selected hyperspherical channels. To this end, we follow the recommendation of Lin,[9] that to solve Eq. (1), the combination of a hyperspherical harmonic basis set and an independent-electron basis set efficiently represents both the small and large regions in R. Using such a basis set, Koyama, Takafuji, and Matsuzawa[10] obtained an adiabatic description of high-lying doubly excited $^1P^\circ$ states up to the $n=7$ threshold. We also employ a similar technique to obtain accurate potential curves for the $^1P^\circ$ symmetry of H^- up to $H(n=12)$. The LS-coupled hyperspherical harmonics[7] involve Jacobi polynomials in $\cos(2\alpha)$ and standard coupled spherical harmonics. The independent-electron basis functions are instead composed of properly symmetrized hydrogenic orbitals. Equation (1) is thus converted to a generalized eigenvalue equation at each value of R, $\mathbf{U}\mathbf{c}_\mu=U_\mu(R)\mathbf{O}\mathbf{c}_\mu$, in which $\mathbf{O}$ is the full overlap matrix. This composite basis displays linear dependence because of its overcompleteness, severely hampering the diagonalization procedure and producing unphysical eigenvalues. To overcome this problem, the Hamiltonian matrix $\mathbf{U}$ is transformed into the representation in which $\mathbf{O}$ is diagonal, while discarding all the overlap eigenvalues corresponding to null solutions of the eigensystem. The total basis set is thus orthogonalized at each R, in a stable and automatic fashion. As a rule of thumb, the total number of basis functions in the new transformed representation increases by unity for every 10 a.u. increase in R.

Figure 1(a) shows the adiabatic potential-energy curves generated for the $^1P^\circ$ symmetry of H^- accessed by the photodetachment experiments at LAMPF.[11] For the present calculations, which give these curves up to the $n=12$ hydrogenic threshold, we have used a primitive basis set of 49 hyperspherical harmonics and 123 two-electron orbitals. Since the density of states grows dramatically at high energies and the curves belonging to different manifolds begin to exhibit sharp avoided crossings, we show these potential curves as R-dependent effective quantum numbers $\nu_\mu(R)\equiv[-2U_\mu(R)]^{-1/2}$ vs $\sqrt{R}$. We stress that these potential curves have been plotted *adiabatically*, whereby the closeness of avoided crossings truly reflects weak channel interactions, or approximate symmetry. (Reference 3 gives a molecular in-

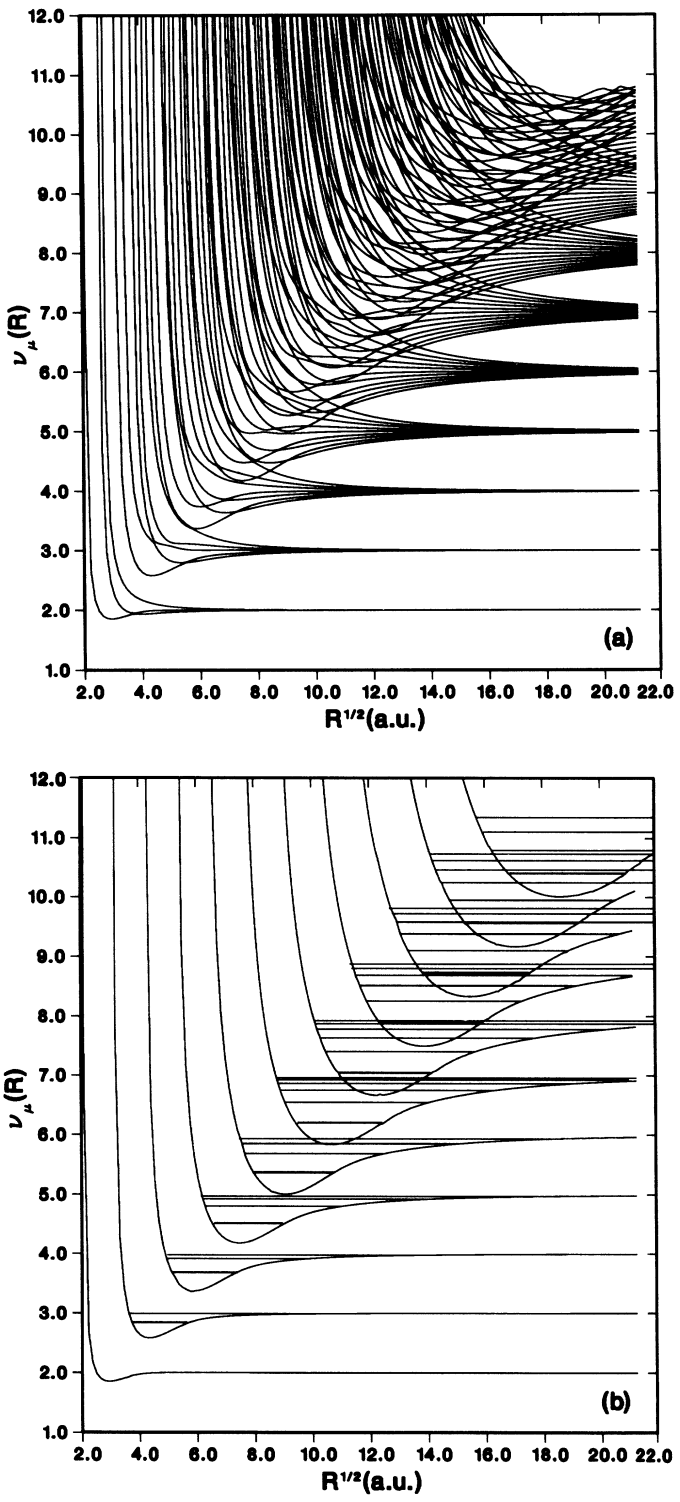

FIG. 1. (a) Adiabatic potential curves for $^1P^\circ$ H^- shown as effective quantum numbers vs $\sqrt{R}$. One should look edgewise along the Wannier ridge line, $\nu_W = 18^{-1/4}\sqrt{R}$, to see the lowest + channels. In (b), only the lowest + channels within each n manifold are plotted along with the level positions in each potential. The Wannier ridge as an imaginary straight line through the avoided crossings is clearly evident in this figure.

terpretation of such diabaticity.) In the asymptotic region, these diabatic channels converge to the dipole potential $-a_{nKT}/2R^2$ produced by the mixing of degenerate angular momentum states of $H(nl)$ due to the electric field of the outer electron. (Here the channel index μ is equivalently defined as nKT.[2]) Equation (38) of Ref. 2 gives an approximate expression for these channel dipole moments $-a_{nKT}$, eigenvalues of the Gailitis-Damburg operator;[12] e.g., for the lowest + channel in each n manifold, $a_{n,n-2,1} \simeq 3n^2 - 23n/3 + 2/3n + 1$ which differs from the exact values[13] by less than 1%. Autoionizing levels lying in each diabatic channel are obtained by matching the inner radial solution to dipole-field functions in the asymptotic region with the aid of single-channel quantum-defect theory.[14]

In Fig. 1(b), we show only the lowest + diabatic channel in each n manifold having $K = n-2$, $T = 1$. Also shown with horizontal marks are the positions of resonances in each channel. We stress that the great complexity of Fig. 1(a) will prove irrelevant for the process at hand, as almost all the physics of H^- photodetachment is contained in the few diabatic channels shown in Fig. 1(b) (in addition to the $n = 1$ curve not shown here).

We also fitted positions of the first resonance in the lowest + channel for $n = 3,4,5$ ($K = n-2$, $T = 1$) by a two-electron Rydberg formula[15] $E(n,n) = -(z-\delta)^2/(n-\mu)^2$, obtaining values for the screening parameter $\sigma = 0.1587$ and quantum defect $\mu = -0.3770$. Combining this Rydberg formula with the dipole scaling law[12,14] relating successive levels within a given potential curve, we arrive at a generalized two-electron formula which describes all the resonance positions observed experimentally (in a.u.),

$$E(m,n) = -\frac{1}{2n^2} - \exp\left[\frac{-2\pi(m-n)}{\alpha_{n,n-2,1}}\right] \times \left[\frac{(1-\sigma)^2}{(n-\mu)^2} - \frac{1}{2n^2}\right], \qquad (2)$$

where $\alpha_{n,n-2,1} = (a_{n,n-2,1} - \frac{1}{4})^{1/2}$, $m = n$ describes the Wannier states,[16] and $m = n+1, n+2, \ldots$ give the dipole states. The doubly excited states calculated using Eq. (2) are compared in Fig. 2 with the experimental resonance positions. A similar fit to the same resonance positions calculated by Ref. 4 gives $\sigma = 0.1629$ and $\mu = -0.3423$. The two fits are indistinguishable on the scale of Fig. 2. The parameters from the second fit are close to those cited in Ref. 11.

The most striking feature in Fig. 2 is that all the experimental Feshbach resonances correspond very closely only to those doubly excited states lying in the + channel for which the quantum number K is *maximum* within a given n manifold, i.e., $K = n-2$, providing concrete evidence for the dominance of the lowest + channel in each hydrogenic series. Furthermore, the higher

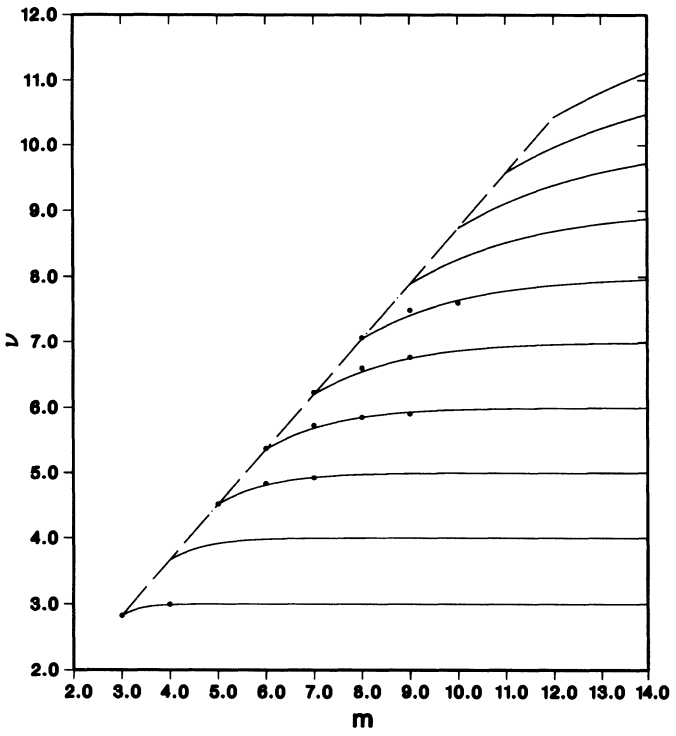

FIG. 2. Feshbach resonances converging on hydrogenic thresholds $H(n)$ shown as effective quantum numbers $\nu = [-2E(m,n)]^{-1/2}$ vs m. The solid lines are from Eq. (2) with the quantum number $m \geq n$ treated as continuous. The intersections of these curves with integer values m define resonance positions. Hyperspherical energies are nearly indistinguishable from these curves. The experimental resonances from Refs. 11 and 24 are given as solid circles whose size is comparable to a typical error bar. The Wannier ridge states having $m=n$ are those for which the dashed line intersects the solid lines.

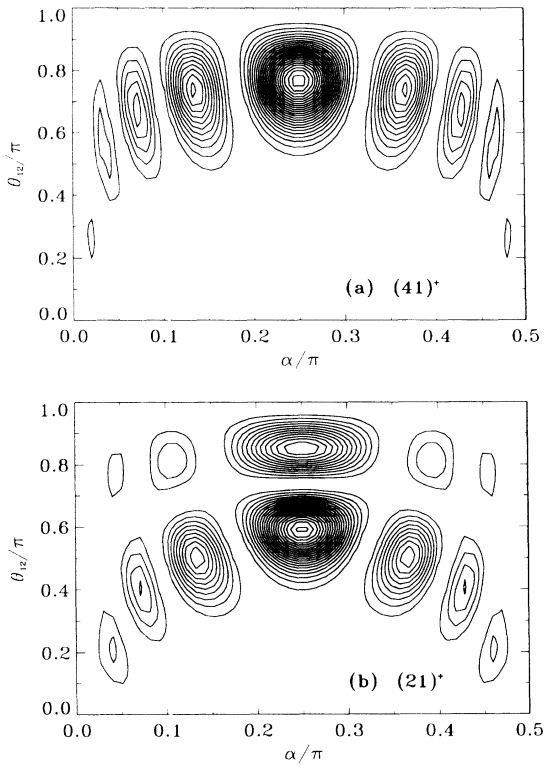

FIG. 3. The adiabatic two-electron density function shown as a contour plot vs α and θ_{12}, displaying the model patterns for the two lowest + channels in the $n=6$ manifold at $R=80$ a.u. (a) and (b) correspond, respectively, to $(41)^+$ and $(21)^+$ channels, i.e., $v^A=0^+$ and 1^+.

resonances in each observed series diverge away from the Wannier ridge line and converge exponentially on the respective hydrogenic threshold following a simple dipole scaling law. Thus, we conclude that *of all the* $2n-1$ *channels in each n manifold, only the lowest* + *channel* $(K=n-2, T=1)$ *influences the photodetachment spectrum of* H^-. In fact, the − Feshback resonance below $H(n=2)$ is the only observed photodetachment resonance[17] in H^- which fails to fit this pattern. (Note that the only + channel in the $n=2$ series has a repulsive dipole barrier which supports a shape resonance.[7]) Experimental studies indicate that the lowest + channel remains largely dominant for helium photoabsorption also,[18] but resonances seen in higher + channels suggest that this dominance is weaker for He than H^-.

Another interesting feature of the experimental data [Figs. 1(a)-1(d) in the preceding Letter] is that the autoionizing states show up as window resonances,[19] indicating that the dipole matrix element to the "bound part" of the resonant wave function is much smaller than the continuum contribution. Resonances, being localized at large R, thus have no physical overlap with the H^- ground state. The main decay mode for these autoionizing resonances appears to be the open + continuum of the next-lowest hydrogenic threshold, at least when energetically allowed.

To interpret the total dominance of the *lowest* + curves, we display in Fig. 3 contour plots of the two-electron density[20] as a function of α and θ_{12}. These plots were obtained at $R=80$ a.u., corresponding approximately to the minima of the two lowest + curves, $(KT)^+=(41)^+$ and $(21)^+$, converging to $H(n=6)$. An immediate observation from these plots is the extra nodal line in θ_{12} for the $(21)^+$ diabatic channel at $\theta_{12}\simeq 0.75\pi$. This would indicate that the d/dR nonadiabatic coupling between these two + diabatic channels should be negligible.[21] As a consequence, high double excitation is achieved through an initial dipole transition into the lowest continua of Fig. 1(b) followed by successive nonadiabatic transitions between the dominant + channels, each having no nodes in θ_{12} similar to that in Fig. 3(a). Accordingly, we propose that the selection rules for the main channel interactions in H^- photodetachment are most simply stated as $\Delta n=-1$, $\Delta A=0$, and $\Delta v=0$, where $v=\frac{1}{2}(n-K-T-1)$ is the bending vibrational

quantum number of the three-body rotor,[22] namely, the number of nodes in θ_{12}. It is the approximate conservation of the v quantum number that serves as the main outcome of this Letter.

We also note that at higher energies the Feshback resonances begin to exhibit new features. The first resonance of the $n=9$ series at $-0.008\,02$ a.u. lies below the $n=8$ threshold. (It remains to be seen whether the experimental structure just visible near the $n=8$ threshold[11] is associated with this resonance.) This has two interesting implications. First, the main decay channel for this resonance is no longer the $n=8$ continuum but the next lowest continuum, namely, the $n=7$. Second, this broad resonance will be strongly perturbed by the narrow dipole resonances of the $n=8$ series lying very close to the $n=8$ threshold [see Fig. 1(b)], as in other familiar multichannel Rydberg spectra.[23] This phenomenon should become more pronounced and even ubiquitous as higher photon energies are reached.

We remark in conclusion that our stable numerical techniques permit computation of adiabatic potential curves for H^- at energies very close to the double-continuum threshold. The resulting analysis, coupled with recent experimental observations, has identified the dominant photodetachment channels for this process.

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