Interfering Resonances: Avoided Crossings of Autoionizing States in Molecules

L. A. Collins and B. I. Schneider
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

C. J. Noble
Daresbury Laboratory, Science and Engineering Research Council, Daresbury, United Kingdom

and

C. W. McCurdy and S. Yabushita
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210
(Received 22 May 1986)

The internuclear separation is used as a continuous parameter to vary the coupling strength between resonances of different autoionizing series in order to study the interference effects and the validity of independent-resonance models. This interference can have profound effects on the autoionization mechanism, which are demonstrated for $e^- + H_2^+$ collisions. The new feature predicted by our calculations is the analog in the resonance case of avoided crossings for bound states and opens new avenues for an understanding of the autoionization process and has interesting experimental implications.

PACS numbers: 34.80.Gs, 34.80.Kw

Resonances play important roles in the description of collisions in atomic, molecular, surface, and nuclear physics.[1-4] Of particular interest are Feshbach or core-excited resonances, which arise from the temporary trapping of the colliding particle in the field of an excited state of the target. These compound states are unstable and decay to a final configuration of the target and scattered particle. However, the trapping produces a time delay in the motion of the continuum particle resulting in an enhancement of the cross section in the vicinity of the resonant energy. This time delay is associated with a lifetime τ or width ($\Gamma \approx 1/\tau$) of the resonant state. Since various autoionization as well as recombination and dissociative processes[5] operate through such resonances, their study is also of great interest to such diverse fields as plasma physics, laser physics, surface physics, and astrophysics.[6] In electron collisions with atomic and molecular ions, the Feshbach resonances lie in Rydberg series that converge on the ionization limits of the compound system. In many cases, different series can overlap and in some instances strongly interfere if the coupling between the various components is large. As first demonstrated by Cooper, Fano, and Prats[7] in their classic study of the effects of correlation on the autoionization mechanism, this interference can dramatically alter the widths and positions of the isolated series. In addition, in certain cases the phenomenon of bound states embedded in the continuum[8] can arise. arise. Therefore, the study of these interfering series is vital to an accurate description of autoionization and its associated mechanisms and to the determination of the validity of certain independent-resonance models. Unfortunately, in most cases, the relative positions of the series are fixed, obviating a systematic study of the interference effects as a function of the coupling strength. What is needed is a continuous variable that changes the relative coupling strengths between the series. For atomic systems, models using an external magnetic field have been invoked. In the case of molecular systems, the internuclear distance R serves a similar purpose and has distinct advantages as the continuous variable since no new external electric or magnetic fields need to be introduced. At each value of R, we perform a set of calculations of the resonant widths and positions for the various series. We can therefore systematically change the relative positions and coupling strengths between the resonant states by simply varying R. While the internuclear distance has been used as a probe of pseudo-bound-state behavior for elastic collisions,[9] this Letter reports its first systematic use to study interference effects among Feshbach resonances below various excited-state thresholds. As an example, we investigate the $^1\Pi_u$ resonances below the first excitation threshold ($1\sigma_u$) for electron scattering from the hydrogen molecular ion H_2^+ as a function of the internuclear distance R since this symmetry exhibits the most dramatic interference effects.

We have performed scattering calculations using four different approaches: (1) the R-matrix method,[10] (2) the complex-basis-function method,[11] (3) the close-coupling linear-algebraic method,[12] and (4) the effective-optical-potential, linear-algebraic method.[13] In all four approaches, we seek a solution to the Schrödinger equation for the interaction of a continu-

um electron with a single-electron target molecule fixed at R[4]:

$$(H_0 + V_{ee} + V_{en} + T_e)\Psi(1,2) = E\Psi(1,2), \quad (1)$$

with T_e the kinetic energy of the continuum electron and V_{en} (V_{ee}) the interaction between the continuum electron and the nuclei (bound electron). The Hamiltonian describing the target H_2^+ molecule is given by H_0 and has associated eigenstates $\{\phi_n\}$. We expand the total system wave function as

$$\Psi(1,2) = \sum_{n=1}^{m} A(\phi_n(1)F_n(2)) + \sum_{\alpha} \chi_\alpha(1,2)\, d_\alpha, \quad (2a)$$

$$(\phi_n | F_{n'}) = 0, \quad (2b)$$

where A is an antisymmetry operator and F_n is a scattering solution. The first term (P space) includes a summation over a limited number of target states for which scattering information is directly desired while the second term (Q space) is added for completeness. In the close-coupling formulation [close-coupling linear-algebraic method or m-state close coupling mCC)] we include a sufficient number m of target states in the P-space part to guarantee convergence of the resonant parameters; the correlation functions are merely employed to relax the strong orthogonality constraint [Eq. (2b)]. For the other three methods, P space is constrained to a small number of terms of interest while the Q-space part is expanded to include the doubly excited states and their interaction. The Feshbach resonances in the latter case are primarily modeled by the correlation functions while in the CC approach they are represented by the closed channels. We have employed all four methods in order (1) to provide accurate cross comparisons for this sensitive problem and (2) to study the interplay and the convergence properties of the P and Q spaces. Further details of this study will be reported in a future paper.

We are now ready to investigate the effects of coupling (strong interference) on the independent-resonance formulation (IRF). In Fig. 1, we present a schematic representation of the core-excited resonances of H_2^* with respect to the bound states of H_2^+ as a function of R. We are particularly interested in the resonances below the first excited-state threshold ($1\sigma_u$), for which all channels but the elastic are closed, and in their interaction with the resonances lying below the $1\pi_u$ state. Since the $1\pi_u$ state is degenerate ($\pi_u^\pm$), we also have a third series of the form $1\pi_u^- n\delta_g^+$; however, this series plays only a minor role and will be neglected in this exposition but not in the calculations. At internuclear distances beyond the equilibrium for H_2^+ ($R = 2.0a_0$), the second series lies above the $1\sigma_u$ excited state and has little effect on the first series. The lowest state of the first series has the form $1\sigma_u 1\pi_g^+$ and goes to the united-atom limit for He* of $2p3d$ while that of the second series, $1\pi_u^+ 2\sigma_g$, becomes $2s2p$. However, from atomic observations, we know that the $2s2p$ is the lowest-lying resonance for $e^- + He^+$ scattering. Therefore, the two independent series must cross between the united-atom limit and $R = 2.0a_0$. Whether this crossing will result in overlapping or strongly interfering resonances depends on the strength of the coupling between these two series.

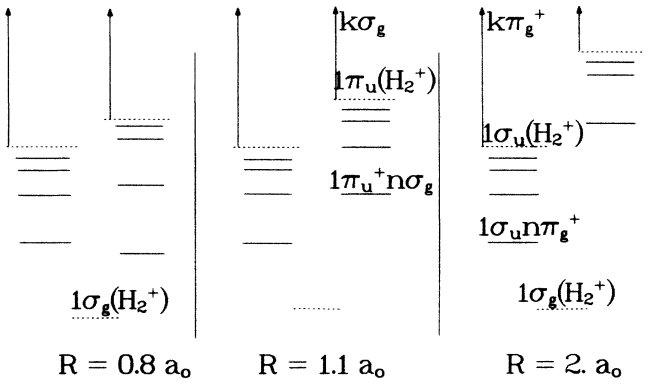

FIG. 1. Schematic representation for the $^1\Pi_u$ symmetry of the $1\sigma_u n\pi_g^+$ and $1\pi_u^+ n\sigma_g$ Feshbach resonance series of H_2^* lying below the $1\pi_u$ threshold for e^--H_2^+ scattering as a function of R. The resonances are depicted by solid lines, the states of H_2^+ by dashed lines.

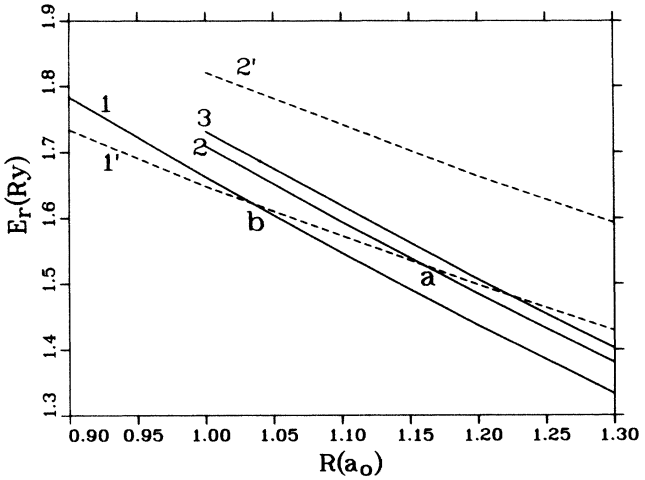

FIG. 2. Resonant position E_r as a function of R for the lowest few $^1\Pi_u$ resonances in the $1\sigma_u n\pi_g^+$ (solid lines) and $1\pi_u^+ n\sigma_g$ (dashed lines) series in 2CC. The numbers give the order of the resonances within each series.

We pursue this model in a more quantitative fashion in the next set of figures. Figure 2 displays the resonant positions E_r of selected states in the two series, $1\sigma_u n\pi_g^+$ (solid lines) and $1\pi_u^+ n\sigma_g$ (dashed lines), calculated in an IRF. In other words, we employed a two-state CC approximation ($m=2$) in each case, a $[1\sigma_g, 1\sigma_u]$ for the first series and a $[1\sigma_g, 1\pi_u^+]$ for the second. Between $R=1.00a_0$ and $1.25a_0$, we observe the lowest resonance state from the second series crossing all of the $1\sigma_u n\pi_g^+$ curves. The $1\sigma_u n\pi_g^+$ series has widths of approximately 3–4 meV while the $1\pi_u^+ 2\sigma_g$ width is of the order of 70–80 meV. If we wish to follow the *lowest*-lying resonance, we start on the $1\sigma_u 1\pi_g$ curve 1 at large R, move in to point b ($R\approx 1.06a_0$), and then switch to the $1\pi_u^+ 2\sigma_g$ curve 1′. The width remains at about 3 meV until b and then suddenly changes to 80 meV ($1\rightarrow 1'$). The second-lowest resonance would be described by curve 2 ($1\sigma_u 2\pi_g$) from large R to point a ($R\approx 1.16a_0$), curve 1′ from a to b, and curve 1 from b to smaller values of R. This behavior of the width as a function of R is depicted in Fig. 3 in the IRF by the solid curves. We now introduce the effects of coupling (dashed curves) between the two series by performing a 4CC calculation $[1\sigma_g, 1\sigma_u, 1\pi_u^{\pm}]$. We observe from Fig. 3 that the effect of the coupling is both to shift the position of the maxima and to broaden the curves. The contrast between the "box" structure of the IRF widths and the broad curves of the fully interfering case lends dramatic support to the necessity of including coupling effects in some overlapping-resonance situations. The enhancement of the resonant width at larger values of R could have profound ramifications for a process like photoionization. The larger width might allow certain transitions that are highly forbidden in the IRF. We thus observe that such interference effects can dramatically alter the resonance structure and substantially effect the scattering.

Finally, in Fig. 4, we present 4CC calculations with the close-coupling linear algebraic method for the widths of the lowest three $^1\Pi_u$ resonances as functions of R. For comparison, we also included several 5CC ($4CC+2\sigma_g$) results for the lowest resonance. All four methods produced results in very good agreement, indicating the efficacy of representing the doubly excited resonances by large Q-space expansions. We note the distinct change in the behavior of the lowest resonance around $R=1.2a_0$. This marks the point at which the dominant configuration changes from $1\sigma_u 2\pi_g^+$ ($R>1.2$) to $1\pi_u^+ 2\sigma_g$. This behavior of the lowest resonance for H_2^+ is unique to the Π_u case. For example, for the Σ_g resonances at large R, the two series are $1\sigma_u n\sigma_u$ and $1\pi_u^+ n\pi_u^-$ with the former lying lower in energy. The lowest resonance of the first series goes to a united-atom limit of $2s^2$ while that of the second series forms a $2p^2$ state. As the $2s^2$ resonance lies lowest, these two resonance curves will not cross. Since the widths of the $1\sigma_u n\pi_g$ series are so small ($\approx$ 3–4 meV), we did not unambiguously observe behavior consistent with bound states embedded in the continuum. The width in the 5CC calculations ($\Gamma \leqslant 1$ meV) does become smaller than that for the 2CC case. However, whether this is anomalous is difficult to judge. A case in which the two series have resonances of almost the same width would provide a better test. The second rise in the width of the third resonance at

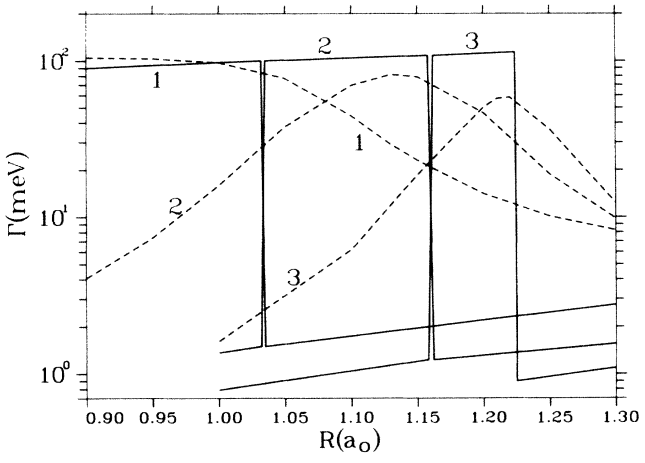

FIG. 3. Resonant width Γ (meV) as a function of R for the lowest three $^1\Pi_u$ resonances. Solid curves, 2CC (independent series); dashed curves, 4CC (fully coupled). The numbers label the order of the resonances in each case.

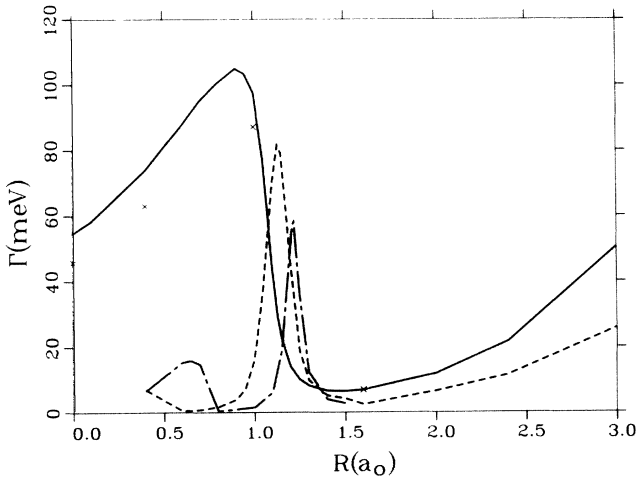

FIG. 4. Resonant width Γ as a function of R for the first (solid curve), second (dashed curve), and third (chain-dashed curve) lowest $^1\Pi_u$ resonances in 4CC; crosses, 5CC.

about $R = 0.6a_0$ represents the crossing of the second $1\pi_u^+ n\sigma_g$ state.

We observe that by changing the internuclear separation for the target molecule we can systematically study the interference effects between two or more series of Feshbach resonances without introducing any new interactions. This provides a valuable tool for assessing the validity of independent-resonance models in both atomic and molecular systems. Whether these effects can be observed experimentally for H_2^+ is another question. Based on simple calculations, we feel that these effects might manifest themselves in the dissociative photoionization of H_2 provided that the target system could be prepared in an excited vibrational state ($v \geq 3$). Certainly the effect is not unique to H_2^+ and would arise for many other molecular systems.

We wish to acknowledge the support of the U. S. Department of Energy through the Los Alamos National Laboratory (for L.A.C. and B.I.S.), the NATO Scientific Exchange Grant No. 687/84 (for C.J.N., B.I.S., and L.A.C.), and National Science Foundation Grant No. CHE-8217439 (for C.W.M. and S.Y.). The assistance of Dr. J. Tennyson on the preliminary R-matrix calculations is gratefully acknowledged.

[1]*Resonances,* edited by D. G. Truhlar, American Chemical Society Series Vol. 263 (American Chemical Society, Washington, D.C., 1984); J. B. Hasted and D. Mathur, in *Electron-Molecule Interactions and their Applications,* edited by L. G. Christophorou (Academic, New York, 1984), p. 403.

[2]N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980); M. A. Morrison, Aust. J. Phys. **36**, 239 (1983).

[3]E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982).

[4]H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); A. M. Badalyan, L. P. Kok, M. I. Polikarpov, and Yu. A. Simonov, Phys. Rep. **82**, 31 (1982).

[5]J. N. Bardsley and M. A. Biondi, Adv. At. Mol. Phys. **6**, 1 (1970); Y. Hahn, Adv. At. Mol. Phys. (to be published); K. Kirby, S. Guberman, and A. Dalgarno, J. Chem. Phys. **70**, 4635 (1979).

[6]*Molecular Astrophysics,* edited by G. H. F. Diercksen, W. F. Huebner, and P. W. Langhoff, NATO Advanced Study Institutes Series C, Vol. 157 (Reidel, Dordrecht, 1984).

[7]J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Lett. **10**, 518 (1963).

[8]H. Friedrich and D. Wintgen, Phys. Rev. A **32**, 3231 (1985).

[9]W. Domke, J. Phys. B **16**, 359 (1983).

[10]P. G. Burke, I. Mackey, and I. Shimamura, J. Phys. B **10**, 2497 (1977); J. Tennyson and C. J. Noble, J. Phys. B **18**, 166 (1983).

[11]C. W. McCurdy, in *Resonances,* edited by D. G. Truhlar, American Chemical Society Series Vol. 263 (American Chemical Society, Washington, D.C., 1984), p. 17.

[12]L. A. Collins and B. I. Schneider, Phys. Rev. A **27**, 101 (1983).

[13]B. I. Schneider and L. A. Collins, J. Phys. B **18**, L857 (1985), and Phys. Rev. A **33**, 2982 (1986).