PHYSICAL REVIEW
LETTERS

VOLUME 28 24 APRIL 1972 NUMBER 17

Short-Lived Resonant State of H^{--}†

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(Received 13 March 1972)

A short-lived resonant state with configuration $(2s)^2(2p)\ {}^2P^o$ is computed for H^{--} using the stabilization method. The resonant energy is 14.8 eV and the estimated width is roughly 1 eV, all in excellent agreement with experiment.

In a recent experiment, Walton, Peart, and Dolder[1] have measured the intensity of non-state-selected hydrogen atoms produced when a beam of H^- ions is crossed with a beam of electrons. They report a resonance structure in the 14–15-eV region and estimate the resonance center to be at 14.5 eV with an energy scale uncertainty of ± 0.2 eV. The value for the resonance center is essentially an estimate since no line-shape analysis has been done.

If a resonance is found in the reaction $e + H^- \rightarrow H + 2e$, H^{--} must be formed since an electron is absorbed into H^-. Further, if this resonance breaks up by ejecting two electrons, in order to conserve energy, one electron must drop down to an orbit of lower principal quantum number. This is exactly as in autoionization. Hence, we can conclude that if "two (electrons) go out, one must go down and three must have been up"; i.e., the resonant state has three electrons with principal quantum number greater than one. The obvious configurations are $(2s)^2(2p)[{}^2P^o]$, $(2s)(2p)^2$-$[{}^2S^e, {}^2P^e, {}^2D^e]$, and $(2p)^3[{}^2P^o, {}^2D^o]$. We have chosen as the most likely configurations the $(2s)^2(2p)$ and $(2p)^3\,{}^2P^o$.

The method chosen to compute the resonance was the stabilization method.[2,3] With the stabilization method one chooses a basis of functions which he guesses will span the bound portion of the resonant wave function. The diagonalization will fit the basis as best it can to the continuum wave functions. If the guess is good, the diagonalization will only be able to make a good fit close to the nucleus at the resonant energy. Therefore, as the basis is extended, all of the eigenfunctions from the diagonalization procedure will change drastically except at the resonant energy, where the fit is already good. A one-electron basis of five s and five p Slater-type orbitals was chosen with a single exponent, and a matrix Hartree-Fock (HF) calculation was attempted for the configuration $(2s)^2(2p)$. The self-consistent-field procedure converged to the HF orbitals for exponents 0.75–1.05. Outside of this range, convergence was difficult or impossible indicating that the span of the basis was outside of the localization of the wave packet. When convergence could be obtained, for each different exponent, a configuration-interaction calculation was done with all contributing configurations made from the first three s and first three p HF orbitals. There were 67 of these configurations. Of the 67 eigenfunctions, in all cases, only two had a total weight (sum of squares of coefficients) on $(2s)^2(2p)$ and $(2p)^3$ larger than 0.05, one with energy above and one below the HF energy. The stabilization method says that the resonant wave function is the one which is the most localized and least coupled to the other determinants. Therefore, the exponent for the *s* function and the exponent for the *p* function were varied independently until the total weight on the $(2s)^2(2p)$ and $(2p)^3$ configurations of the lower eigenfunction mentioned above was maximized. This resulted in a wave function with exponents $\zeta_s = 0.99$ and $\zeta_p = 1.05$ whose energy was 14.8 eV above the ground state of H^- and which was 66% $(2s)^2(2p)$ and 29% $(2p)^3$. The remaining 5% was distributed among the other 65 configurations, presumably in an attempt by the diagonalization procedure to fit the continuum portion of the exact scattering wave function. Ideally, of course, all ten exponents should have been varied independently, but this would not have been feasible computationally. Some experimentation with this, however, has indicated that while it is possible to change the distribution of weights between the $(2s)^2(2p)$ and $(2p)^3$ configurations [shifting most of the weight to $(2s)^2(2p)$], their total weight and the resonant energy are not changed significantly.

The calculation also showed the possibility of another resonance at higher energy and probably with a largely $(2p)^3$ wave function. The $(2s)(2p)^2$ configuration was not studied.

Although possible,[4] the width of the resonance is difficult to calculate because of the boundary-condition problem. Experience with stabilization calculations on model problems[3] has shown that a good estimate can be obtained from the range of energies about the resonant energy for which a stabilized wave function can be found. This band of wave functions forms the wave packet. This yields an estimate of about 1 eV which is in qualitative agreement with the experiment (which is also not accurate).

The resonance discussed above might be difficult to compute by standard coupled-channel methods. Energetically all bound states of hydrogen are open channels giving an infinity of three-body, final channels. This difficulty emphasizes the advantages of the stabilization method which never calculates anything but integrals between bound-state functions and can use all the experience and programs of stationary-state calculations. If the resonant energy alone is to be determined, the boundary conditions are not important. However, since the HF orbitals are not very different from hydrogenic orbitals, then from our earlier argument that the third electron must go down as two go out, it is difficult to imagine the hydrogen atoms produced as being in anything other than the ground state. This argument could be checked by repeating the e^--H^- crossed-beam experiment with state selection of the hydrogen atoms. If the above argument is correct, then the resonance should be seen almost exclusively in the ground-state channel.

The authors are grateful to R. K. Nesbet and the IBM Corporation for supplying us with the computer programs, and to G. A. Segal for several enlightening discussions and suggestions concerning the HF convergence problem.

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†Work supported under National Science Foundation Grant No. 53-4815-2095.

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