A LOW-LYING RESONANCE IN THE SPECTRUM OF H⁻

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Abstract—It was proved by PEKERIS[1] that the singly excited states of H⁻ lie exactly at, or slightly above, the ground state of hydrogen. Using a theory of FANO,[2] these fictitious states will have a configuration interaction with the H⁻ continuum. The strength of this configuration interaction is computed for the mixing of a $1s2p\ ^1P^0$ state with the H⁻ continuum for different values of the fictitious binding energy of the $2p$ valence electron. In every case, the effect of the configuration interaction is to induce a rapid change of the phase shift of the continuum wave function by a quantity of $\pi/2$ over an energy range of a few times 0.01 eV, at an energy somewhat above the hydrogen ground state. The variation from $\pi/2$ to π is much slower. Such a swift change of the phase shift may be identified with the occurrence of a low-lying shape resonance.

1. INTRODUCTION

RESONANCES in $e^- - H$ scattering have been reviewed by BURKE[3] and by MASSEY and BURHOP.[4] Such a resonance or intermediate compound negative-ion state is for the H⁻ ion similar to a doubly excited state for He. These doubly excited states have been subjected to many investigations, starting with BRANSDEN and DALGARNO[5] to the most modern one, based on a close coupling with correlation approximation, which is also included in Burke's review. BOTTCHER[6] has translated the method of Brandsen and Dalgarno into the case of $e^- - H$ scattering and—inherent to the variational method he used—finds upper limits for the energies of the resonances which are significantly higher than the energies obtained from close coupling approximations. However, these upper limits will readily come down with an increasing number of parameters in the variational method.

Using a theory of KAPUR and PEIERLS[7] for nuclear resonances, HERZENBERG and MANDL[8] have computed positions and widths of resonances in H⁻. Their result also includes a low-lying resonance, but the determination of position and width is very uncertain. Just as any other member of the He iso-electronic sequence, H⁻ will possess the following features:

(i) a ground state $1s^2$;

(ii) series of continua, $H(n)+e^-$, in which n is the principal quantum number of the electron in neutral hydrogen;

(iii) for $n \geq 2$, series of doubly excited states, called closed-channel resonances, which converge to $H(n)$.

It is shown in this paper that the fact that, in the closed-configuration approximation, the singly excited states of H⁻ lie exactly at, or a little above $n = 1$, does not necessarily imply

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that these singly excited states will have no effect on the spectrum. In fact, a singly excited state will mix with the H^- continuum in order to form a low-lying so called shape resonance. We shall investigate this configuration interaction in some detail.

2. THE INTERACTION OF ONE DISCRETE STATE φ AND A CONTINUUM $\psi_{E'}$.

The essence of the theory of the effect of configuration interaction on intensities and phase shifts (Fano[2]) may be described by the following sentences:

We consider one discrete non-degenerate state with normalized wave function φ and energy E_φ. In our case, we consider the $1s2p^1P_1^0(m = 0)$ state of H^- with an energy exactly equal to or slightly more than -1 Ry. (Pekeris[9]). We consider further a continuum. This continuum is described by a set of normalized, non-degenerate wave functions $\psi_{E'}$, which depend on the continuous variable energy E'. Moreover, E_φ lies in the interval covered by E'. We want to diagonalize the energy matrix which belongs to the states φ and $\psi_{E'}$ in order to obtain the energies E and the wave functions Ψ_E of the mixed system. Here E and Ψ_E are given as the solutions of the secular equation

$$H_{op}\Psi_E = E\Psi_E, \tag{1}$$

where H_{op} is represented by a square matrix of infinite rank, viz.,

$$\lim_{n \to \infty}$$

H_{op}	φ	$\psi_{E_1'}$	$\psi_{E_2'}$	$\psi_{E_3'}$	$\cdots$	$\psi_{E_n'}$
φ	E_φ	$V_{E_1'}$	$V_{E_2'}$	$V_{E_3'}$	$\cdots$	$V_{E_n'}$
$\psi_{E_1'}$	$V_{E_1'}^*$	E_1'	0	0	$\cdots$	0
$\psi_{E_2'}$	$V_{E_2'}^*$	0	E_2'	0	$\cdots$	0
$\psi_{E_3'}$	$V_{E_3'}^*$	0	0	E_3'	$\cdots$	0
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$		$\vdots$
$\psi_{E_n'}$	$V_{E_n'}^*$	0	0	0	$\cdots$	E_n'

$$\tag{2}$$

In the limit as n goes to infinity, each value of E in the half-closed interval E' is a solution of equation (1). One may say that the mixing of a discrete state to a continuum does not change the energy range of this continuum. In order to evaluate the matrix (2), it is necessary to compute the following quantities:

$$(\varphi|H|\varphi) = E_\varphi,$$

$$(\varphi|H|\psi_{E'}) = V_{E'}, \tag{3}$$

$$(\psi_{E'}|H|\psi_{E''}) = E'\delta(E' - E'').$$

Equation (1) is solved with the aid of a method due to Dirac.[10] Assuming the continuum wave functions $\psi_{E'}(r)$ to have the usual boundary condition $\psi_{E'}(r) \xrightarrow[r \to \infty]{} \cos(k(E')r + \delta)$, an extra phase shift Δ is added to δ as a consequence of the configuration interaction;

$$\Delta = -\arctan\frac{\pi}{z(E)}, \tag{4}$$

where

$$z(E) = \frac{E - E_\varphi - F(E)}{|V_E|^2} \tag{5}$$

$$F(E) = \int_{E'_{min}}^{E'_{max}} \frac{|V_{E'}|^2}{E - E'} \, dE'. \tag{6}$$

If, at a certain value of E, say E_R, Δ varies rapidly with energy from 0 to π, taking a value of $\pi/2$ at E_R, then E_R is the value of the energy of a resonance. In this case it is a shape resonance because the most important decay mode, i.e. the radiationless transition into the continuum $1s2p \rightarrow 1s \infty l$, is not forbidden. Passing through E_R, the quantity $\pi/z(E)$ has to vary from a value very small compared with unity through infinity at $E = E_R$ and very sharply again to a very small value, but with opposite sign. This description is required in order to produce a swift variation of Δ. The position of the resonance is thus given by the solution of

$$E = E_\varphi + F(E). \tag{7}$$

The width of the resonance may be identified with the width of the interval in which Δ changes by approximately π (VAN KAMPEN[11]).

3. DETERMINATION OF THE WAVE FUNCTIONS

The equations of the preceding section will be solved in spherical co-ordinates (r, θ, φ). It should be noted that $\psi_{E'}$ must represent the first continuum of H⁻. This is a hydrogenic 1s electron plus an outgoing plane wave in the z-direction with an energy of k^2 Rydberg units. The continuous variable k^2 can take all positive values from zero to infinity. The plane wave $\exp(ikz)$ is a solution of the equation

$$\Delta f + k^2 f = 0. \tag{8}$$

For the normalized wave function of the bound hydrogenic electron, the exact expression

$$u_{1s} = R_{1s}(r)Y_{00}(\theta, \varphi) = \frac{\exp(-r)}{\sqrt{\pi}} \tag{9}$$

applies. The value of the corresponding energy parameter E is $E(1s) = -1$ Ry. Thus, in the absence of any interaction between the ground-state electron of the hydrogen atom and the free electron, one obtains as the wave functions $\psi_{E'}$ the expression given by MASSEY and BATES:[12]

$$\psi_{E'}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2\pi}} [e^{ikz_1 - r_2} - e^{ikz_2 - r_1}], \tag{10}$$

where

$$z = r \cos \theta \tag{11}$$

and $E' = k^2 - 1$ are the eigenvalues of the equation

$$H_{op}\psi_{E'} = E'\psi_{E'}. \tag{12}$$

The interaction of $1s2p\ {}^1P_1^0$ with the anti-symmetrical form of equation (12), which represents the continuum triplet states, is of course zero because the configuration interaction between singlets and triplets vanishes. The wave function φ of $1s2p\ {}^1P_1^0$ could have been evaluated with arbitrary precision by using a method due to Pekeris (SCHIFF et al.[13]). Pekeris has shown that singly excited H^- wave functions may be constructed with bound characteristics. However, it is difficult to define what is meant by the notion of binding energy for these bound states. For H^- one obtains

$$(\varphi|H|\varphi) \gtrless -1\ Ry. \tag{13}$$

From this relation, PEKERIS[1] concludes that H^- has no singly-excited states. However, the configuration interaction between φ and $\psi_{E'}$ will induce a singly excited feature in the H^- continuum with the quality of a resonance. The obtained resonance will enhance the continuous absorption strength in a relatively small energy range in a similar way as shown by KIVEL[14] for molecular nitrogen. Using Pekeris-type wave functions requires an enormous amount of numerical work. Moreover, the Pekeris-type wave functions are expressed in perimetric co-ordinates so that—in order to find the quantity V_E—one would have to express the continuum wave functions in such co-ordinates. For these reasons, in preliminary studies, one may conceive the fictitious bound $1s2p$ state of H^- (fictitious, because it will interact with the continuum in which it is inbedded) as a hydrogenic core electron which is almost in the ground state and a $2p$-electron with a certain fictitious negative energy ε. This value of ε is in one way difficult to interpret but, on the other hand, it certainly exists because otherwise it would be impossible to construct a Pekeris-type wave function with bound characteristics. For instance, the value of ε would be zero in the oversimplified description of the bound wave functions of two-electron systems for which two screening constants are used to minimize the energy (ECKART[15]). In this case, the bound wave function has lost its bound characteristics and is thus useless. Since the wave functions have to be non-degenerate, we must use one of the states of $1s2p\ {}^1P_1^0$, say the state with $m = 0$, which can be represented by a wave function φ_0. Because of their angular dependence, the two other states, with $m = \pm 1$, will be found to have zero interaction with the continuum. Thus we write

$$\varphi_0 = \frac{1}{\sqrt{2}}(u_{1s}(\bar{r}_1)u_{2p}(\bar{r}_2) + u_{1s}(\bar{r}_2)u_{2p}(\bar{r}_1)), \tag{14}$$

where

$$u_{1s}(\bar{r}) \approx R_{10}(r)Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{\pi}}\exp(-r), \tag{15}$$

and

$$u_{2p}(\bar{r}) = R_{2p}(r)Y_{10}(\theta, \varphi) = R_{2p}(r)\sqrt{\frac{3}{4\pi}}\cos\theta. \tag{16}$$

A good approximation to $R_{2p}(r)$ is then given by the normalized, screened hydrogenic function

$$rR_{2p}(r) = P_{2p}(r) = \frac{\sqrt{Z_{eff}}}{2\sqrt{6}}(Z_{eff}r)^2\exp(-Z_{eff}r/2) \tag{17}$$

with

$$Z_{eff}^2 = -n^2\varepsilon = -4\varepsilon. \tag{18}$$

In order to evaluate the small value of the fictitious energy ε, one may argue qualitatively as follows. The method outlined by PEKERIS[16] for evaluating wave functions of two-electron systems consists in calculating the energies of wave functions with correct asymptotic behaviour. If one includes enough terms in the expansion of the wave function, one can approach the true wave functions and energies as close as desirable. The method includes implicitly mutual polarization of the electrons, incomplete screening of the action of the nucleus and any discrete-discrete configuration interaction. However, discrete-continuum interaction is never included in the expansion. The method gives very satisfactory results but for H^- one obtains bound wave functions with a total energy for the configuration of slightly more than -1 Ry. This result can only be interpreted as meaningful if the $1s$-electron has lost a small amount of its energy because of the presence of a $2p$-electron. The $2p$-electron turns out to be weakly bound in this description. We will make an estimate for the fictitious binding energy of the $2p$ electron.

If one assumes the first term in the Pekeris-expansion to represent the situation in which the valence electron is still unbound, one obtains for the total energy of the ground state of H^- exactly the same result as with the aid of the Ritz principle in the evaluation of a ground state wave function with only one screening constant (ECKART[15]), namely,

$$E = -(Z - \tfrac{5}{16})^2 2\ \text{Ry} = -0.945\ \text{Ry}. \tag{19}$$

In other words, one finds one $1s$-electron with 0.945 Ry as binding energy while the other $1s$ electron is still unbound. It is known that the real value of the energy lies below this value by an amount of $\Delta E = 0.110$ Ry. Thus, as a consequence of the occurrence of higher-order terms in the expansion, both $1s$-electrons have got an extra amount of energy equal to half of (-0.110)Ry. Hence, one may consider 0.055 Ry as being the binding energy of the $1s$ valence electron.

Following the same reasoning for the $1s2s\,^3S$ term in H^- (PEKERIS[9]), one obtains

$$E = -0.743\ \text{Ry and thus } \Delta E < 0.257\ \text{Ry}. \tag{20}$$

The binding energy of the $2s$-valence electron, and thus also of the neighbouring $2p$ electron, will thus be no larger than a fraction of 0.257 Ry. The maximal value of ε is half of -0.257 Ry, i.e., approximately -0.13 Ry. However, we have made the calculations for $\varepsilon = -0.05$, -0.01 and -0.005, respectively, in order to cover a set of possibilities, but even smaller values of the fictitious binding energy are possible and even probable. In particular, we find $\varepsilon = -0.005$ for the fictitious binding energy of the $2p$-electron is about $\frac{1}{10}$ of the binding energy of the valence $1s$-electron in the ground state. The fraction $\frac{1}{10}$ is estimated from extrapolation along the He iso-electronic sequence. The formulae given in the next section are general and thus also applicable for very small absolute values of ε, if it should prove to be desirable to use these.

4. A LOW-LYING SHAPE-RESONANCE IN THE SPECTRUM OF H^-

With the assumptions of the preceding sections, one can calculate the bound–free configuration interaction in H^- in a straightforward analytical way. The result is

$$V_{E'} = \frac{Z_{\text{eff}}^{7/2}\sqrt{(\pi/2)}}{k[(Z_{\text{eff}}^2/4) + k^2]^2}\left[1 - i\frac{(Z_{\text{eff}}^2/4) - 3k^2}{(Z_{\text{eff}}^2/4) + k^2}\right] \quad \text{if } k \neq 0. \tag{21}$$

Thus

$$|V_{E'}| = \frac{Z_{\text{eff}}^{7/2}\sqrt{\pi}}{4k[(Z_{\text{eff}}^2/4)+k^2]^3}\,(Z_{\text{eff}}^4 - 8Z_{\text{eff}}^2 k^2 + 80k^4)^{1/2}. \tag{22}$$

The quantity $\log_{10}|V_{E'}|$ is shown in Fig. 1 for different values of Z_{eff}. The quantity $F(E)$ can be computed easily from the relation

$$F(E) = \int_{E'_{\min}}^{E'_{\max}} \frac{|V_{E'}|^2}{E-E'}\,dE' = \frac{Z_{\text{eff}}^7 \pi}{16} \int_{\delta}^{\infty} \frac{Z_{\text{eff}}^4 - 8Z_{\text{eff}}^2 k^2 + 80k^4}{k^2(E+1-k^2)[(Z_{\text{eff}}^2/4)+k^2]^6}\,d(k^2). \tag{23}$$
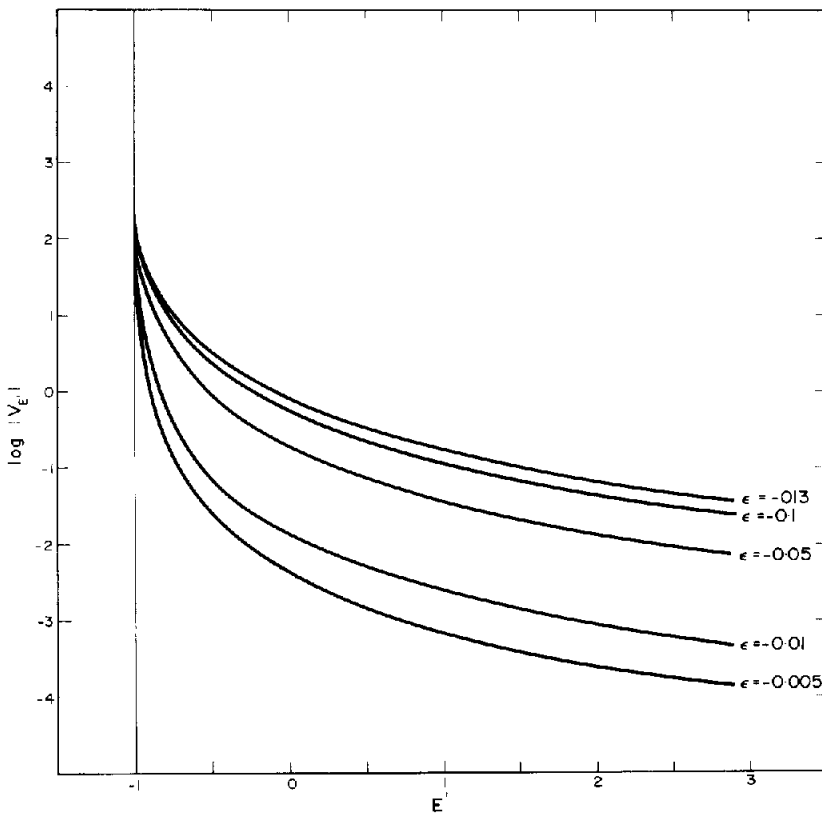

FIG. 1. The logarithm of $|V_{E'}|$ to the base 10 is shown as a function of the position in the H⁻ continuum for different values of the fictitious binding energy $(-\varepsilon)$.

In equation (23), δ is the energy interval in which the continuum wave function has mainly an s-character as a consequence of the interaction of the hydrogenic $1s$-electron with the slow-moving free electron because the lowest-lying parts of the H⁻ continuum will mix with the fictitious $1s2s$ states. The $1s2p$ wave function will thus be orthogonal with respect

to the continuum wave functions in this energy range. The phase shift Δ was calculated from equations (4), (5), (22), and (23) for different values of δ; the results are shown in Figs. 2 and 3. We find a swift variation, over an energy range of a few times 0.01 e.v., from 0 to $\pi/2$ at an energy slightly above $(-1 + \delta)$, followed by a smooth variation from $\pi/2$ to π. The resonance will thus, by decay, give rise to a broad asymmetrical spectral line with a steep wing in the red. Since this is a feature which has been observed in diffuse interstellar lines (BRÜCK et al.[18]) and since moreover the diffuse interstellar lines are just like the hydrogen atom distributed rather uniformly over space, we present our result as evidence for identification of these lines with bound-bound transitions in H⁻, as has already been suggested by RUDKJØBING and co-worker.[19,20,21,22] If this interpretation is correct, and in order to obtain a reasonably small resonance, one sees from Figs. 2 and 3 that small absolute values of ε have to be preferred. The exact position of the resonance will, however, only be obtained after a calculation with more exact wave functions is performed.

5. CONCLUSIONS

A formula is given for the calculation of the bound-free configuration interaction in H⁻ if the binding energy of the bound state is known. It is, however, difficult to define this fictitious binding energy exactly. The suggestion made by Rudkjøbing for identifying some
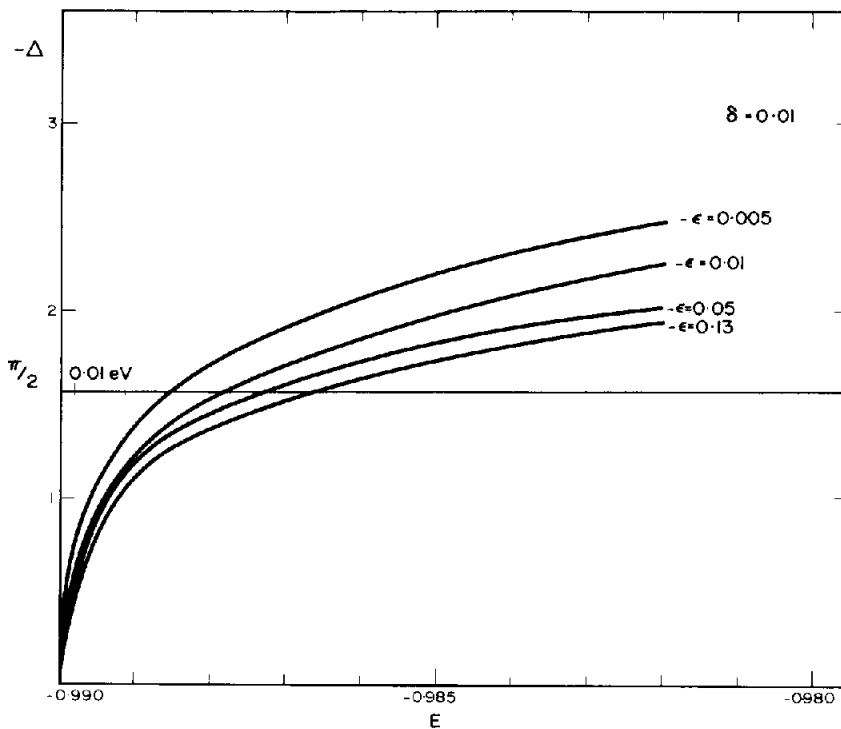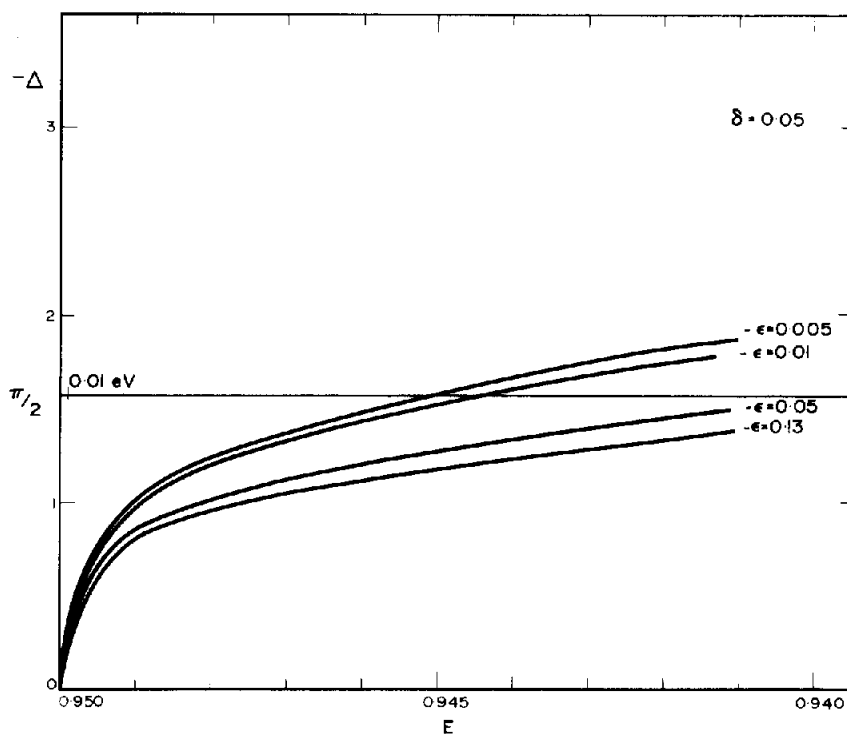

FIG. 2. The phase shift Δ of the wave function Ψ_E of the mixed system, as a function of energy, for $\delta = 0.01$ and different values of the fictitious binding energy $(-\varepsilon)$.

FIG. 3. The phase shift Δ of the wave function Ψ_E of the mixed system, as a function of energy, for
$\delta = 0.05$ and different values of the fictitious binding energy $(-\varepsilon)$.

diffuse interstellar lines as transitions in H⁻ finds some support in our results. The result
is that a broad asymmetrical shape-resonance is induced in the lower parts of the H⁻
continuum when an $1s2p$ state of H⁻ is mixed with the first H⁻ continuum. The transition
$1s2p \rightarrow 1s^2$ will thus give rise to a broad asymmetrical line, as has been observed by Brück
et al. on diffuse interstellar lines. On the other hand, any discrete-continuum configuration
interaction yields broad asymmetrical features, as has been shown by Fano.

In order to obtain a decisive result, we plan to repeat this calculation with the aid of the
best available Pekeris-type wave functions for the discrete state and a more accurate ex-
pression for the continuum wave function. The Pekeris-method describes the two-electron
system as a whole, without determining the energies and wave functions of the electrons
separately. This method will avoid the difficulty of introducing a fictitious binding energy
$(-\varepsilon)$.

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