Theoret. chim. Acta (Berl.) 16, 63—74 (1970)

Calculations on Some Excited States of He$^-$

I. ELIEZER
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

Y. K. PAN
Department of Chemistry, Boston College, Chestnut Hill, Massachusetts

Received July 5, 1969

The stabilization technique has been used to examine several possible resonance states for He$^-$. Stabilized roots have been obtained at 0.43, 19.3, 20.3, 21.2, 57.3 and 58.3 eV. These results are discussed and compared to experimental values.

Die Stabilisierungstechnik wurde benutzt, um verschiedene mögliche Resonanzzustände für He$^-$ zu untersuchen. Dabei ergaben sich stabilisierte Wurzeln der Säkulargleichung bei 0,43, 19,3, 20,3, 21,2, 57,3 und 58,3 eV. Die Ergebnisse werden diskutiert und mit experimentellen Werten verglichen.

La technique de stabilisation a été utilisée pour examiner quelques résonances possibles pour He$^-$. Des racines stabilisées ont été obtenues à 0.43, 19.3, 20.3, 21.2, 57.3 et 58.3 eV. Ces résultats sont discutés aux valeurs expérimentales.

1. Introduction

The phenomena of double electron excitation in helium and of autoionization in rare gas spectra were already under study some thirty years ago both experimentally [1, 2], and theoretically [3, 8], and thus are not exactly new. Of late, after the subject had lain dormant for many years, there has been an intense revival of interest in quasi-stationary states of helium, i.e., states above the first continuum threshold. The reason usually given is that new experimental techniques have been developed in the last few years, permitting the accumulation of new and precise data. It seems to us that an equally important reason has been the development of the theories of scattering in physics and of the quantum mechanics of the excited and continuum states. This has provided a conceptual framework serving to coalesce the various measurements into a general picture and provide a directional impetus for further experimental studies. Helium, of course, is the natural choice being the simplest system available with more than one electron (except for H$^-$ [5]). A major effort so far has gone into inelastic scattering which has resulted in a doubly excited auto-ionizing target. These target states can, of course, also be studied by photon absorption spectroscopy which helped greatly in their elucidation. An increasing number of experiments have indicated compound state formation which in the case of helium means negative ion formation. These states, being adjacent to, or embedded in, a continuum are autoionizing, i.e. quasi-stationary (assuming, of course, the proper symmetry and other quantum numbers). This qualitative interpretation of a growing body of data is widely accepted by now but relatively few quantitative calculations have been made. The efforts were directed at several objectives – to calculate the energy values of the states, or resonances as they are commonly called, to compute the widths and to determine the line shapes. This paper will be concerned with the first objective, i.e. the calculation of the energies at which these resonances are to be expected. One possible scheme for such predictions has been worked out recently [4]. The present work starts from these ideas and presents a quantitative treatment of the He^- system which leads to energy values agreeing reasonably well with most of the experimental data on He^- resonances available.

2. The Experimental Data

For a long time all investigations of quasibound states formed in the scattering of electrons off helium (as well as by other mechanisms of excitation of neutral helium) were confined to excited states (mostly doubly excited) of neutral helium, which are formed by the reaction $e^- + He \rightarrow e^- + He^*$, where the incident electron plays a passive role. As late as 1955 Holøien and Midtdal [8] wrote that the species He^- was generally considered as non-existent, although some experimental studies [7] had hinted at its presence.

The initial impetus leading from the above situation to the present state of knowledge of a plethora of He^- quasibound states seems to have been provided by the work of Schulz and Fox [8]. An analysis of these results [9, 10], led to the postulated existence of a "compound helium atom" as it was called, meaning a negative helium ion. Following this suggestion, Schulz measured the elastic scattering of electrons off helium with a greatly improved energy resultion. As is well known, he obtained a sharp resonance in the cross section below the excitation threshold of the $1s2s$ helium states [11, 12]. His final result for the energy of this state was [13] 19.30 ± 0.05 eV above the ground state of helium. Similar, though less exact results were obtained by Fleming and Higginson [14] and by McFarland [15]. The existence of this resonance has since been amply confirmed by several investigators such as Simpson and his co-workers [16, 17], and Golden and his collaborators [18, 19].

Once the idea of the existence of transient He^- ions causing resonances in scattering was established and the experimental techniques developed, i.e. elastic and inelastic scattering and transmission cross-section measurements with adequate energy resolution and detection, experiments were carried out over a wide range of energies and the 19.3 eV resonance was revealed to be far from an isolated phenomenon. Kuyatt *et al.* found [17] no less than nine resonances (or structures) in the range 19–24 eV in transmission experiments, and also indications of two resonances in the 60 eV range. The resonances in the 19–24 eV range were also the object of angular distribution studies, [13 a, 36, 65], while the resonances in the 60 eV range were confirmed and examined in more detail by Simpson and co-workers [20]. Schulz and Philbrick found [21] an additional two resonances in inelastic experiments in the range 20–23 eV. Chamberlain *et al.* in inelastic experiments [22, 29] confirmed Schulz's findings and extended the energy range examined, while improving the resolution. They found four additional resonances and also reconfirmed the existence of the two resonances below 60 eV. They also found indications of several other resonances. The obvious conclusion was that the occurrence of resonances in the scattering of electrons by helium is not confined to any particular energy range but is a general phenomenon and that such negative ion states are always connected with the (singly and doubly) excited states of helium. Other resonances have been found below the $n = 3$ and 4 levels of helium.

In the meantime a large body of experimental data accumulated on resonances and compound state formation in other atomic and molecular systems but this is beyond the scope of the present article. Suffice it to say that He^- resonances are examples of the general reaction

$$e^- + P \rightarrow P^{-*} \begin{array}{l} \nearrow e^- + P \quad \text{(Elastic scattering)} \\ \searrow e^- + P^* \quad \text{(Inelastic scattering, excitation processes).} \end{array}$$

(Transmission experiments observe the total effect of all such processes.) Here the incident electron does not play a passive role but a resonant state of the target particle plus this electron is formed. The experimental technique involves looking for peaks in the scattering cross section or for variations in the transmitted current as a function of the incident electron energy. For further information the reader is referred to some recent reviews [4, 24, 25, 69, 70].

The most controversial resonance observed experimentally was also, strangely enough, the first one to be observed, although without any realization of its meaning at the time. This resonance is the so-called "single particle" He^- resonance. It was observed by Schulz in an elastic scattering experiment [28] at an energy of 0.45 eV. This result has aroused controversy among both experimentalists [18, 19] and theoreticians [24, 25, 69, 71]. However, already back in 1929 Ramsauer and Kollath observed [29] what we would call today a resonance in the cross-section of electrons scattered by helium at 0.75 eV. And in 1935 Normand also found [30] a resonance in this region although his value is 1.1 eV. It must be borne in mind, of course, that the margins of error in these older experiments were rather large.

3. Some Previous Theoretical Treatments

As early as 1936, calculations on the negative helium ion were carried out by Wu [31]. He arrived at the conclusion that the $1s^2 2s\,^2S$ state of He^- would be unstable but that the $1s2s^2$ He^- state should be observable. Similar calculations were recently carried out by Propin [32] (see below).

The hypothesis of the formation of a negative ion as a shortlived species was first put forward by Baranger and Guerjuoy [9, 10]. They predicted the existence of a $1s2s^2S$ state of He^-, above the $1s2s$ helium threshold, with a lifetime of 10^{-15} sec. Their basic assumption of a He^- ion was proved correct by Schulz's experiments [11–13] although these showed a resonance below and not above threshold and with a lifetime nearer $10^{-13} - 10^{-14}$ sec.

In 1961 Ross and Shaw predicted [33] from effective range theory a sharp resonance in the elastic channel below the inelastic threshold and in 1962 Burke and Schey's [34] close-coupling calculations were found to lead to exactly such a type of resonance – below the first excitation threshold. Although they dealt with H^-, their arguments were applicable also to helium. A qualitative explanation was given by Schulz [11] who suggested that the 19.3 eV resonance was due to the interference of potential scattering with the compound negative helium ion state. The question of the configuration of this negative ion state was discussed [16] by Simpson and Fano who concluded that the state is formed by the addition of a $2s$ electron to the $1s2s$ excited helium state and so suggested that the 19.3 eV quasibound He^- state is a $1s2s^2\,{}^2S$ state.

Kuyatt *et al.* tried [17] to provide a semiquantitative theoretical framework to the nine resonances which they observed (see previous section) and calculated from an extremely simplified model a series of energies for the negative helium ion states. Surprisingly, they got a considerable measure of agreement with some of their experimental results, but of course not with all. These, however, are rather crude calculations based on analogies with the helium atom.

Fano and Cooper examined [35] the possible configuration for the two resonances in the 60 eV vicinity and by an identification procedure which combines elements of spectroscopy and collision theory arrived at the assignment of $2s^2 2p\,{}^2P$ and $2s2p^2\,{}^2D$ for these states.

A tool which is being used more and more for the assignment of configurations to the various He^- states is the measurement of angular dependence of the scattering cross-section. Such measurements were first carried out by Erhardt and coworkers for the 19.3 eV He^- state [36, 13a] and by an analysis of their results they arrived at a conclusion identical with that of Simpson and Fano: that this is a ${}^2S$ state and the configuration is probably $1s2s^2$ formed by the addition of an electron to the $2\,{}^3S$ and $2\,{}^1S$ excited states of helium. They also found resonances at energies of 19.9 eV, 20.45 eV (${}^2P$) and 21.00 eV (${}^2D$). From 21.5 to 24 eV the angular dependence was nearly unchanged with energy.

Simpson *et al.* carried out [20] angular distribution experiments for the 57.1 and 58.2 eV helium resonances. After an analysis of their results they concluded that their angular dependence observations "are not inconsistent" with the assignment of $L=1$ and $L=2$ respectively to the above resonances.

Theoretical quantum mechanical calculations of the energies of the quasibound negative helium ion have been rather few. Two attempts were made by Zhikareva to treat the 19.3 eV resonance as a Breit-Wigner type with coupling in three channels [37, 39]. The first – a $1\,{}^1S - 2\,{}^3S - 2\,{}^1S$ calculation led to a value of 17.8 eV, while the second, on the assumption of a P wave, led to a value of 19.2 eV which according to the author represents a metastable $1s2s2p\,{}^2P$ state of He^-. Inclusion of the $3s$ channel and the study of the P wave shows a resonance that could well be one of those reported in Ref. [23] just below the 3^3S state of He [38a].

Recently Kwok and Mandl [39], using a variational principle, obtained a narrow ${}^2S$ resonance in the He^- system just below the first excited state of helium. The energy was calculated to be 19.5 ± 0.15 eV which is surprisingly good in view of the relatively crude wave functions which they used.

As mentioned above, variation calculations were carried out by Propin [32] in 1961 on the energies of the $1s2s^2\,{}^2S$, $1s2s2p\ {}^2P$, $1s2p^2\,{}^2S$ and $1s2p^2\,{}^2D$ states of the negative helium ion but the calculations are not sufficiently accurate to be of value for comparison with the resonance scattering experiments. Very recently, Young [72], carried out similar calculations obtaining fair agreement with the energies of some of the resonances seen by Kuyatt [17].

The most reliable calculations to-date are those of Burke and co-workers [40] who used the close-coupling method, took account of all the $n = 2$ channels and obtained a multiresonance structure for the 19 – 22 eV region, the essential feature of which was the large polarizability of the $2\,^3S$ and $2\,^1S$ states due to the neighbouring $2\,^3P$ and $2\,^1P$ states. They obtained, in addition to the ^2S resonance at 19.3, a ^2P resonance at 20.2 eV and a ^2D resonance at 21.0 eV. However, although they obtained an excellent value for the S-wave resonance: 19.33 eV, they failed to obtain agreement with the experimental width by an order of magnitude. They also detected the $2\,^2S$ resonance at 19.9 eV reported in Refs. [65] and [23]. The position of the $2\,^2P$ and the $2\,^2D$ resonances are reasonably well calculated in the present paper and in Ref. [40] when compared to the experimental results of Ref. [65]. The $2\,^2P$ (19.45 eV) resonance reported in Ref. [15] and [17], calculated in the present paper and, approximately, by a close-coupling method in Ref. [38], is completely missing from the calculations of Burke *et al.* This is disturbing because both the latter two papers use close-coupling methods.

To conclude this section – a few words on the resonance at 0.45 eV, which at present seems to be the most intriguing. There have been some calculations of the cross-section in this range by LaBahn and Callaway [42, 43, 73], O'Malley [44], Kestner *et al.* [28] and Husain [27] but they were concerned with the general shape of the curve and their calculations show no resonance (although Kestner *et al.* do mention this possibility). Burke *et al.* [40] also report that they find no trace of this structure. Few explanations have been offered as yet [24, 25, 69, 71]. One should note for future discussion that theoretical attempts to "see" this structure have so far been based on looking for a change by π in the phase shift. This of course assumes that the structure would be caused by a single isolated relatively narrow resonance.

4. Method of the Present Calculations and Results

In the calculation of energies and wave functions of compound states like the negative helium ion, the problem is that the usual variation method cannot be used, because of the existence of an infinite number of states of lower energy having the same symmetry as the resonance states. These states are the ground state of the target plus a free electron with a continuum of energy values, having the proper angular momentum. Therefore, a variational calculation without any restrictions, no matter how careful, will always result in the absence of compound states.

The close-coupling method avoids this problem by seeking to solve for the scattering cross-section at all energies, off and on resonance, by what could be termed a continuum state, as opposed to bound state, method. Phase shifts at all energies are calculated for all exit channels. This method is, of course, the most direct and when it can be carried out efficiently (in the sense of computer time) and accurately it yields by far the most information. At present the method suffers from the computational difficulty of not being able to treat large numbers of states, non-spherical and many (more than three) electron systems. Also its success off resonance is not so impressive (because of truncation problems) as its success near resonance energies.

On the other hand some investigators [47–58] omit any treatment of the cross-section and use quasi-stationary methods for calculating the energies, wave functions and (sometimes) widths of the resonances. There are several such calculations on two electron systems. The only ones on three electron systems are those by Bardsley, Herzenberg, and Mandl [56] and Eliezer, Taylor, and Williams [41, 50] on H_2^-, and by Kwok and Mandl [39] on He^- as mentioned above. These methods sacrifice information on potential scattering off resonance for the relative advantage of making the problem resemble stationary bound state problems. With this advantage the whole machinery of quantum chemistry, atomic and molecular spectroscopy can be carried over enabling one to study the resonance features of bigger and more complicated systems.

A scheme of obtaining resonant state trial functions together with a quasi-stationary method for calculation of their energies was proposed recently by Taylor *et al.* [4, 70]. Resonant states were classified as Type I core-excited (CE 1), which lie close below the parent excited states, Type II core excited (CE 2) which lie close above or among the parent excited states, and single-particle resonances (SP), which lie close above the parent ground state. The CE 1 (also called Feshbach, compound state or hole-particle) resonances are considered to be formed by the virtual process of the incoming electron exciting one of the electrons of the target and becoming temporarily trapped by the slight potential well formed by the additional amount of nuclear charge to which it is exposed when the target core electron moves away. The CE 2 (or "shape") resonances are considered as virtual states of the potential well caused by core-excitation, i.e. "long-lived" localized wave-packets [70]. The SP resonances are the result of an extension of the CE 2 argument [70]: if an excited target state can support virtual levels, it should be possible for the ground state to do so also. The potentials here are shallow due to the relatively small polarizability of the ground state. SP resonances are expected to be very broad.

The method of calculating the resonance energies is basically a C.I. method (using the $N+1$ electron Hamiltonian). Several trial configurations selected on the basis of experimental results and physical ideas are chosen as the initial wave function of the quasibound state. This is then improved by adding more configurations of bound functions until it is observed that one root and one trial eigenfunction is no longer affected by the addition of any bound function configurations with which it could mix. The root is termed "stabilized" and taken as representative of a resonant state. The eigenfunction corresponding to the root is the resonant wave function. The rationale of the method is given in Ref. [4] and [70]. The method is obviously an approximate one but it does lead to *ab initio* calculations of values which are found to approach reasonably closely the experimentally observed resonant energies.

The calculations in the present paper were carried out using a modified Harris-Taylor-Williams [60–64] program. In this program trial functions are composed of linear combinations of products of one-electron orbitals. The first step in such a process is the selection of a one-electron basis set which we now describe. First it should be noted that the one electron functions do not necessarily have to be eigenfunctions of one electron angular momenta. All that is required of an *exact* atomic wave function is that it be an eigenfunction of total orbital and spin angular momentum. Therefore, the highly flexible orbitals described in Ref. [41] could be used. Each orbital is described by five indices (α, δ, n, m, v) (see Ref. [41] for details). The orbital function is such that if $\alpha=\delta$, $n=m=v=0$ one has a 1s type orbital. The combination of two orbitals both with the same $\alpha=\delta$ but one with $m=1$, $n=v=0$ and the other with $n=1$, $m=v=0$ give a 2s orbital etc. In other words, by free variation of parameters in the procedure we shall shortly describe to pick one-electron functions, one can get 1s, 2s, 2p etc., type functions if the variation procedure decides that these represent the most rapidly converging set. On the other hand, as might be expected since finite size sets are used in any real problem, the ideal sets of orbitals may not be necessarily like 1s, 2s, etc. In fact they are usually distorted orbitals. To be sure, the lowest orbitals that make up the main configuration of any linear combination of α configurations that represent a state do turn out to be close to 1s, 2s and 2p orbitals. The higher orbitals, though, are not necessarily of atomic type and are quite distorted. For these reasons, we shall refrain from calling our orbitals by an "nl" name (1s, 2p, etc.) and use "ln" instead, i.e. $s1$, $s1'$, ..., $p2$, $p3$ ... etc.

The one-electron orbital basis was chosen as follows: A $z=2$ hydrogenic 1s orbital was taken as $s1$. A second s type orbital was then added and both orbitals were varied to make the best one term ground state for He. This gave $s1$ and $s2$. The first p-type orbital, $p2$, was obtained by adding a p-type orbital to the $s1$ orbital and varying it to minimize the $s1p2$ state energy. Higher orbitals were constructed by minimization of higher roots of the secular equation with the trial function $\sum_{n=2}^{N} C_n s1\,ln$ holding the first $N-1$ orbitals fixed. The set of orbitals obtained is listed in Table 1. Products of three of these orbitals were then used as a basis for the He^- calculations. The roots were checked while adding additional configurations and the stabilizing roots were selected as the resonance energy values. This method seemed most reasonable for studying the resonances near the $n=2$ level of helium, since the first few sn and pn orbitals were like orbitals in the field of the He^+ ion.

For the calculation of the single particle (0.45 eV) resonance the procedure was slightly modified. As this resonance is considered to be an electron in the field of the slightly polarized ground state core, the first step was again a variation treatment of the ground state of helium, but in addition some account was taken of the above mentioned polarization by allowing variation of the core orbitals in the field of the third electron. The three-electron wave functions were then formed by adding the orbitals given in Table 1, one by one, to the helium ground state function and again the roots obtained were checked at each stage for stabilization. The SP resonance was found to be a $s1s1'$ wave function times a one-electron orbital that was a linear combination of $s3$ to $s6$. This mixing of four configurations to get stability reflects two things. First is the relatively large width of the single particle resonance as compared to the CE 1 and CE 2 functions. Second and probably more important is that no simple way exists for choosing one term (as opposed to a linear combination of terms) orbitals because any energy minimization method of an electron orbiting a helium atom will always just give a helium

Table 1. *S and P basis orbitals*

Orbitals	δ	α	n	m	v
$s1$	2.16741	2.18528	0	0	0
$s1'$	1.20055	1.17383	0	0	0
$s2$	0.66421	0.22036	1	0	0
$s2'$	0.32915	0.49373	0	1	0
$s3$	0.33297	−0.07843	2	0	0
$s4$	0.46900	−0.75000	3	0	0
$s5$	0.28028	−0.23898	4	0	0
$s6$	0.21977	−0.28893	4	2	0
$s6'$	0.43100	0.02413	2	4	0
$p2$	0.53331	0.56032	0	0	1
$p3$	0.30448	0.21947	1	0	1
$p4$	0.22304	0.33456	0	1	1
$p5$	0.21877	−0.06120	2	0	1
$p6$	0.25762	0.38643	3	0	1

Table 2. *Comparison of experimental and theoretical results on quasistationary states of* He^-

Experimental energy	Ref.	Configuration	Previous calculations	Ref.	Present results	
					Energy	State
19.30 ± 0.05	[11–13] [17, 36, 72]	$1s2s^2$	17.8 19.3 19.5 19.7	[31] [40] [39] [72]	19.3	^2S
19.47	[15, 17]	$1s2s2p$	19.2	[38]	19.6	^2P
20.45 ± 0.05	[17, 65]	$2\,^2P$	20.2	[40]	20.3	^2P
21.00 ± 0.05	[17, 65]	$2\,^2D$	21.0	[40]	21.2	^2D
57.1 ± 0.1	[17, 20, 22]	$2s^2 2p$			57.3	^2P
58.2 ± 0.1	[17, 20, 22]	$2s2p^2(^2D)$			58.3	^2D
0.45	[26]				0.43	^2S

atom and a free electron. Since the orbitals we used were good for an electron in the field of He^+ it is not surprising that stabilization required three of them to represent a good "outer" electron orbital. Addition of stabilizing configurations did not change the root corresponding to the SP resonance appreciably. Further details of the methods of calculation are found elsewhere [41, 64]. The *S*, *P*, *D* quantum numbers listed in the last column of Table 2 were obtained by inspection of the resulting eigenfunctions.

It should be mentioned that several energy levels of some simple atoms were calculated rather accurately some time ago using a basis set similar to the one described above [61–63].

The results of our calculations are compared with previous theoretical calculations and with selected experimental values in Table 2. It will be seen that the agreement of the present calculations with experiment is fairly satisfactory in all cases.

5. Discussion

As the field of helium resonances is still in a state of flux, there are few facts that are established beyond doubt. Experimentally the resonance whose position has been most accurately and repeatedly established is the resonance at 19.3 eV. In fact this resonance is already being used for energy scale calibrations. The second resonance below the $n=2$ threshold is controversial. Kuyatt *et al.* have observed it at 19.43, it might also have been observed by McFarland whose value is 20.3 and by Fleming *et al.* who give 19.4 eV. However, it is more probable that this last value is a less accurate observation of the 19.3 resonance. Numerous works on the 19.3 resonance do not mention seeing this peak even though its position should make it hard to avoid when studying the 19.3 line shape. In analogy to the $n=3$ and $n=4$ thresholds it might be expected that the $2\,^3S$ threshold would also have an S and P peak below it. However, Burke and co-workers do not see such a peak in their theoretical results. In the present study a ^2P root was obtained at 19.6 eV, but it stabilized rather poorly. The existence of this state is therefore unclear

As to the resonances at 20.4 and 21.0 eV our agreement with experiment [65] and other theory [40] for inelastic scattering to the $2\,^3S$ level is quite good. One can moreover speculate that the broad peak at about 21.2 eV in the work of Chamberlain and Heideman [23] is due to a mixture of both the broad $2\,^2P$ and $2\,^2D$ resonances already seen in the $2\,^3S$ channel.

Another interesting effect is the 19.9 ± 0.05 eV resonance observed by Ehrhardt *et al.* [65] in the $2\,^3S$ channel. This small peak at threshold was also seen in Ref. [23]. A similar peak appears in the $2\,^1S$ channel. The angular dependence of the former peak is definitely S wave [65]. In the present work this resonance was not detected. The following argument could explain this discrepancy: Near an S threshold one would expect from de Broglie wave length arguments that S wave scattering should be dominant. Therefore let us assume that at threshold the rise in cross section is caused by almost pure S wave direct excitation and that higher waves do not come into the direct excitation till a slightly higher energy. As this S contribution rises, it is cut off by destructive interference with the P resonance at 20.45 eV with the result that a peak appears. This peak would have an S angular distribution and would be experimentally indistinguishable from a resonance. A similar explanation could explain the small peak at the beginning of the $2\,^1S$ channel. These structures do seem to be theoretically deduced from close-coupling calculations [40].

There is little to be said about the 57.1 eV and 58.2 eV resonances which seem to have reached a state of consistent measurement, calculation and interpretation.

The 0.45 eV resonance is clearly a problem. We have calculated it at 0.43 eV with configuration $1s1s'S\,^2S$ i.e. a large orbit S electron outside a polarized core. We have already noted in an earlier section that other theoretical attempts dealing with this energy region do not find this structure. It has even been claimed [70], that no S wave single particle resonance should be expected. There are also some experimental results which report the absence of this resonance in observations of total (which should be elastic at this energy) cross section [18, 19]. One can only speculate that, in spite of claims to the contrary, as discussed in Ref. [4], this type of attenuation experiment might be insensitive to small signals. Let us also point out that a similar single particle resonance for H_2^- observed by Schulz in dissociative attachement and in inelastic vibrational excitation has not been observed in Ref. [19]. This latter resonance has been repeatedly theoretically verified [56, 57, 41] by quasistationary methods. In the calculation of the 0.43 result other almost stable roots showed up. Whether these would qualify as resonances is doubtful since they were obviously very broad and completely overlapping. The interesting speculation that arises from this observation is that there may be in the low energy region several broad overlapping resonances and that as a result the resonant structure, though still due to a state of the "internal Hamiltonian" i.e. still a pole of the S matrix, is not associated with a change by π of the phase shift. Similar overlapping structure was also noticed in the calculation of the low SP H_2^- resonance [41].

As we mention later, the stability method has the inherent danger, because of truncation and basis set problems, of being capable of arriving at stable roots that are not physical. Without a calculation of width we would not know this. We believe that the probability of a coincidence causing an error to give a $1s\,1s'S\,{}^2S$ structure with a 0.43 eV stable root is small and we tend to believe in the existence of this structure.

Another intriguing effect associated with the SP resonances and for which evidence has shown up in calculations of both the H_2^- [41] and He^- SP resonances is a level inversion effect. This means that orbits of larger radius have lower energy, giving rise, at low energy, to a possible inverted Rydberg series with the majority of levels packed against the zero of energy and overlapping so thoroughly as to be meaningless from the point of view of calling them resonant levels. The $1s\,1s'S^1$ seems to be the top of this series. Although this effect is far from proven it is not unlikely if one realizes that for core excited resonances and most atomic and molecular problems the electrons see attractive core potentials, resulting in a normal level sequence, while in the SP case it is likely that the electron sees, on the average, a repulsive potential which would favor larger orbits having lower energies (viz. repulsive and attractive potential curves). There is also some evidence of such an effect in preliminary studies of H^- [87, 88]. The level inversion effect is known in analogous situations in molecular orbital theory. For example it is well known that in the Hückel benzene energy level scheme the non-bonding levels (repulsive) have an inverted structure from the bonding (attractive) levels. In diatomic M.O. theory when p electron atoms come together one gets a $\sigma_g - \pi_u - \pi_g - \sigma_u$ level scheme. Note that the $\sigma_g - \pi_u$ is the "normal" order and corresponds to bonding and the $\pi_g - \sigma_u$ is inverted and corresponds to repulsion of the atoms. However, admittedly, level inversion, overlapping levels and the 0.43 eV resonance are still open questions. It should be pointed out that the fairly sophisticated calculations presented here are not the only way to obtain theoretical indications of the SP He^- resonance. A calculation carried out using the formulae [66] for the unrestricted H.-F. ground-state energy obtained with an inverse nuclear charge perturbation method, has yielded the value of 0.48 eV for the He^- ground state energy.

In conclusion, it should be cautioned that although the above stabilization technique will usually give good results for the experimentally observed resonances, it has to be used with great care in the prediction of resonances. Difficulties may arise because although every resonance will result in a stable root in the calculation, it is not entirely certain that every stabilizing root corresponds to a real resonance. Further work on widths should prove of value in this respect. Also, although in principle, this method is applicable to larger systems (a program outline based on this method has been written to deal with systems containing up to 20 electrons), calculations on systems with larger numbers of electrons would be somewhat cumbersome and time-consuming. Nevertheless we feel it can be applied with profit.

Acknowledgement. The author is greatly indebted to H. S. Taylor for helpful discussion and criticism. The computations were carried out on the CDC 3400 system of Tel-Aviv University.

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Prof. I. Eliezer
The Institute of Chemistry
Tel-Aviv University
Ramat-Aviv, Israel