Triply excited ^2P and ^2D resonance of He^-

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The ^2P ($2s2s2p$) and ^2D ($2s2p2p$) resonance structure observed in the electron-helium scattering experiments has been investigated using a saddle-point technique. For ^2P we obtain for the energy $-0.796\,93$ a.u. with an 82-term wave function. This agrees well with the experimental result. In the past, the ^2D structure was thought to be a Feshbach resonance. In this calculation, we show that the $2s2p\ ^3P$ target is repulsive to the third p electron in the sense that the variational energy of the He^- system is monotonically increased as the p electron approaches the target. Hence, the Feshbach resonance cannot be formed for this state. Some comments will be made concerning earlier theoretical calculations in the literature.

I. INTRODUCTION

The triply excited resonances of electron-helium scattering were first reported by Kuyatt *et al.*[1] In this experiment two resonant structures were observed in this energy region. They were analyzed by Fano and Cooper.[2] The lower resonance which occurs at 57.1-eV incident energy is assigned to be a $2s2s2p\ ^2P$ state. Based on the reported position from the $2s2p\ ^3P$ threshold and by elimination of possibilities, the upper structure at 58.2 eV is assigned to be a $2s2p2p\ ^2D$ resonance. Owing to the proximity to the ^3P threshold, the likelihood of this being a threshold effect is, nevertheless, mentioned.[2] In many subsequent experiments[3-8] the existence of these resonances has been repeatedly confirmed. Theoretically, various methods are used to examine these resonances,[9-14] for example, the stabilization method,[9,14] the projection-operator method,[10] and close-coupling calculations.[11] The results generally support the experimental finding.

In the present work, the ^2P and ^2D resonances are studied with a saddle-point technique.[15] We first assume the resonances to have the configuration $2s2s2p\ ^2P$ and $2s2p2p\ ^2D$ with a $1s$ vacancy within the system. Using LS coupling and a multiconfiguration interaction wave function with the vacancy built into it, the Feshbach resonance is searched for variationally. The resonance energy is shown to be a maximum for the parameters in the vacancy orbital and a minimum for all other parameters in the total wave function. The resulting energy gives the best approximation within the inner-shell-vacancy picture, i.e., with square-integrable wave functions.[15] This method, with the continuum neglected, is most suitable for calculating Feshbach resonances, but not suitable for shape resonance.

II. THE WAVE FUNCTION

For the electron-helium system, the nonrelativistic Hamiltonian takes the form

$$H=-\sum_{i=1}^{3}\left(\frac{\nabla_i^2}{2}+\frac{2}{r_i}\right)+\sum_{i<j}^{3}\frac{1}{r_{ij}}, \tag{1}$$

where atomic units are used. The wave function is the product of the radial, angular, and spin parts, which are given, respectively, by

$$\phi_{mnk}(r_1,r_2,r_3)=r_1^m r_2^n r_3^k e^{-\alpha r_1}e^{-\beta r_2}e^{-\gamma r_3}, \tag{2a}$$

$$Y^{l_3,LM}_{l_1l_2;l_{12}}(\hat{r}_1,\hat{r}_2,\hat{r}_3)=\sum_{m_1m_2m_3\mu}Y^{m_1}_{l_1}(\hat{r}_1)Y^{m_2}_{l_2}(\hat{r}_2)Y^{m_3}_{l_3}(\hat{r}_3)\times\langle l_1l_2m_1m_2|l_{12}\mu\rangle\langle l_{12}l_3\mu m_3|LM\rangle, \tag{2b}$$

and

$$\chi(1,2,3)=[\alpha(1)\beta(2)\mp\alpha(2)\beta(1)]\alpha(3)-(1\mp1)\alpha(1)\alpha(2)\beta(3), \tag{2c}$$

where the Clebsch-Gordan coefficients and spin functions α,β are defined in the usual manner.[16] The $\mp$ are chosen such that the total wave function satisfies the Pauli-antisymmetry principle. Hence, if the core electrons form a singlet then the $-$ is used; if triplet, the $+$ is used. α,β,γ, are the nonlinear parameters to be minimized. Combining Eqs. (2), the basis functions become

$$\psi^{l_1l_2l_{12}l_3}_{mnk}(\vec{r}_1,\vec{r}_2,\vec{r}_3)=\phi_{mnk}(r_1,r_2,r_3)\times Y^{l_3,LM}_{l_1l_2;l_{12}}(\hat{r}_1,\hat{r}_2,\hat{r}_3)\chi(1,2,3). \tag{3}$$

For the Feshbach resonances of interest, the vacancy within the system is the $1s$ orbital. In order to build it into the wave function, we assume

$$\phi_{1s}(\vec{r}) = 2q^{3/2} e^{-qr} Y_0^0(\theta, \phi), \tag{4}$$

where q is a parameter to be optimized. The total wave function with the $1s$ vacancy takes the form

$$\Psi = A \sum C^{l_1 l_2 l_3}_{mnk} [1 - P(1)][1 - P(2)][1 - P(3)] \times \psi^{l_1 l_2 l_3}_{mnk}(\vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{5}$$

where $P(i) = |\phi_{1s}(\vec{r}_i)\rangle\langle\phi_{1s}(\vec{r}_i)|$, and A is the antisymmetrization operator. Equation (5) can often be simplified, for example, if l_1 is the only s orbital in the wave function; Eq. (5) may be reduced to

$$\Psi = A \sum C^{l_1 l_2 l_3}_{mnk} [1 - P(1)] \psi^{l_1 l_2 l_3}_{mnk}(\vec{r}_1, \vec{r}_2, \vec{r}_3). \tag{6}$$

To use this wave function for the energy calculation, we first minimize the expression

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{7}$$

with respect to the linear parameters C to obtain the secular equation. The eigenvalue of the secular equation is then minimized with respect to α, β, γ and maximized with respect to q.

III. $2s2s2p\ ^2P$ OF He^-

To test the effectiveness of the saddle-point technique for triply excited states, we first calculated the $2s2s2p\ ^2P$ resonance of He^-. This is the lowest resonance below the doubly excited threshold. Since it is a three particle system various angular components may contribute to the energy. For convenience, the notation $[(l_1, l_2)^k l_{12}, l_3]$ is used to represent a particular angular component. Here l_{12} is the combined angular momentum of l_1 and l_2, and k is the multiplicity of the l_{12} core. For the ^2P state, some possible angular components are $[(s,s)^1S,p]$, $[(p,p)^1S,p]$, $[(d,d)^1S,p]$, $[(s,p)^1P,s]$, $[(d,d)^3P,p]$, etc.

By using a 36-linear-parameter wave function and three angular components $[(s,s)^1S,p]$, $[(p,p)^1S,p]$, $[(s,p)^1P,s]$, we obtain an energy of $-0.780\,37$ a.u. This energy is lower than the doubly excited $2s2s\ ^1S$ of helium. It is a theoretical confirmation of the existence of the ^2P Feshbach resonance. The parameter q in the vacancy orbital is found to be 1.96. If a 10-term $[(p,d)^1P, s]$ component is added to the wave function, the energy becomes $-0.793\,66$ a.u. A 55-term calculation with $[(d,d)^1S,p]$ included gives $-0.795\,13$ a.u. Further inclusion of $[(p,d)^3P,s]$ and $[(p,p)^1P,p]$ with 72 terms gives $-0.796\,69$ a.u. The final result $-0.796\,92$ a.u. is obtained with $[(d,f)^1P,s]$ also included in an 82-term wave function. The nonlinear parameters are optimized to be $\alpha = 0.78$, $\beta = 0.72$, $\gamma = 0.72$, respectively. Relative to the ground-state energy of helium $-2.903\,724$ a.u. (Ref. 17) this resonance is at about 57.33 eV.[18] This is to be compared with the experimental result of Kuyatt *et al.*[1] at 57.1 ± 0.1 eV, and Sanche and Schulz[4] at 57.16 ± 0.05 eV.

In choosing the various angular terms for the He^- system, the singlet core is used more often than the triplet core. This is because the exchange terms for the triplet core and the third electron tend to be positive hence contributes less to the

TABLE I. ^2P $(2s2s2p)$ energy of He^-.

	Author (Ref.)	Method	Energy (eV)
Theory	Elizer and Pan, Ref. 9	Stabilization	57.3
	Nicolaides, Ref. 10	Hartree-Fock and Projection operation	57.3
	Ahmed and Lipsky, Ref. 12	Expansion	57.37[a]
	Smith *et al.*, Ref. 11	Close-coupling	56.48
	Safronova and Senashanko, Ref. 13	2nd-order perturbation	56.65[a]
	Present work	Saddle-point technique	57.33[a]
Experiment	Kuyatt *et al.*, Ref. 1		57.1 ±0.1
	Quemener *et al.*, Ref. 8		57.15±0.04
	Grissom *et al.*, Ref. 7		57.21
	Sance and Schulz, Ref. 4		57.16±0.05
	Golden and Zecca, Ref. 3		56.7/56.93

[a] The energy is converted from atomic unit using helium ground-state energy $-2.903\,72$ a.u., $R_y = 13.6058$ eV.

binding of the third electron.

As compared with the earlier theoretical work of Safronova and Senashenko,[13] Ahmed and Lipsky,[12] and Smith *et al.*,[11] the present calculation gives a more accurate result. Our result agrees well with that of Nicolaides,[10] and Eliezer and Pan.[9]

It is worthwhile to mention that in a Feshbach-resonance calculation, the reliability of the method can no longer be judged by the resulting energy alone. Both the method of approach and the wave function used are important. To use the present calculation as an example, if the condition on q is relaxed, one can obtain an energy in exact agreement with that of experiment. But this would not be a meaningful result from a theoretical point of view. Table I is a comparison of results from theory and experiments.

IV. He^- $2s2p2p$ ^2D

Unlike the calculation of the ^2P state, more care needs to be exercised in computing the ^2D resonance. This is because experimentally its position lies well above the $2s2s$ ^1S threshold but about 3.8 eV below the second ^1S doubly excited state. It is barely below the $2s2p$ ^3P threshold and about 1.9 eV below $2s2p$ ^1P. These will be important factors to consider in selecting the proper angular terms in a variational calculation.

A triply excited state can be viewed as the attachment of the last electron to a doubly excited core. In electron-helium scattering, the incoming electron excites the helium target into a doubly excited state or states. Since the total energy of the system is less than the excitation energy, the third electron becomes bound. A Feshbach resonance is thus formed. In this case, the interaction potential of the doubly excited target and the third electron must be attractive.

Another important consideration is the lower exit channel. For a resonance to be meaningful, the life time should be much longer than the transit time. For narrow resonances, it is usually many orders of magnitude longer. Hence, if energy-wise the resonance lies in the continuum of a lower exit channel, the quasibound resonant state wave function should be essentially orthogonal to that of the exit channel. If not, it will decay through this exit channel immediately and the life time would become comparable to the transit time.

The lowest doubly excited state of He is at 57.84 eV above the ground state.[19] It is formed by the degenerate $2s2s$ ^1S and $2p2p$ ^1S. If the latter configuration is not included the energy would be about 59.41 eV, which is well above the $2s2p$ ^3P threshold. The existence of this low-lying ^1S implies that the ^2D resonance of interest lies in the $[(2s2s + 2p2p)\,^1S, nd]$ continuum. Since the second ^1S state is too high to have any significant effect in the formation of this ^2D resonance, one must exclude the $[(s,s)\,^1S, d]$ and $[(p,p)\,^1S, d]$ angular terms in the variation calculation. Should these two terms be included in the computation, two consequences may occur: (A) If the wave function is very flexible, the result will be lower monotonically towards the ^1S energy if the d electron is allowed to be further and further away from the nucleus. (B) If one does not use a very flexible wave function either by limiting the number of linear parameters or by using a set of unoptimized nonlinear parameters, the result so obtained will not be very meaningful.

Experimentally the ^2D resonance is found to be at 58.2 ± 0.1 eV by Kuyatt *et al.*[1] and 58.25 ± 0.05 eV by Sanche and Schulz.[4] The observed $2s2p$ ^3P of helium is at 58.34 ± 0.05 eV.[20] Theoretically many calculations have been performed for the ^3P state,[21] the most elaborate is perhaps the one that was done by Bhatia and Temkin[19] using Feshbach formalism. Using a Q operator given by Hahn *et al.*,[22] their eigenvalue for the QHQ operator is $-0.761\,49$ a.u., which corresponds to 58.29 eV. If the continuum is included,[19] the resonance with the shift is about 58.32 eV. One can show that a large part of the shift can be accounted for by the saddle-point technique. For this system it recovers 62% of the shift.[23] Hence the ^3P threshold in the present calculation is 58.31 eV.

For the ^2D $(2s2p2p)$ calculation, many angular components are used, for example, $[(s,p)^3P, p]$, $[(p,d)^3P, p]$, $[(p,p)^1D, s]$, $[(s,p)^1P, p]$, $[(p,d)^1P, p]$, $[(p,d)^3F, p]$, etc. In general, the results behave as follow: If the ^3P core is well represented, then the energy of the state is lowered monotonically towards the ^3P threshold as the average radius of the third electron increases. This can easily be seen by fixing the number of linear parameters and decreasing the value of nonlinear parameter γ [see Eq. (2a)]. A typical result is given in Fig. 1. In this figure, the energy as a function of γ is shown. Three angular components, $[(s,p)^3P, p]$, $[(p,d)^3P, p]$, and $[(s,p)^1P, p]$, with a 46-linear-parameter wave function is used. The limit at $\gamma \to 0$ is -0.7606 a.u. (58.317 eV) which is a very accurate ^3P energy. This implies that the ^3P target state is well represented. The slope of this figure is very steep suggesting that the ^3P target is repulsive to the third electron. This is perhaps due to the exchange interaction which tends to raise the energy of the system substantially. On the other hand, if the ^1P core is well represented instead, there is a minimum of E at approximately -0.744 a.u. (58.78 eV) in a 63-term wave function

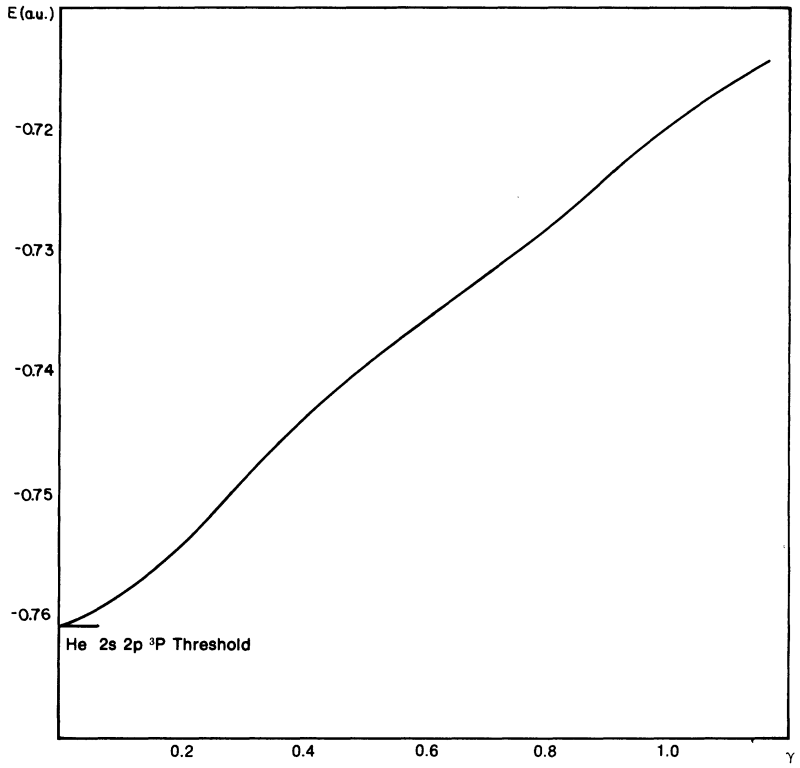

FIG. 1. Resonance search for $^2D(2s2p2p)$ state of He^- (in a.u.). The wave function used has 46-linear-parameters with $\alpha=1.0$, $\beta=9.6$, $q=1.92$. The angular component includes $[(s,p)^3P,p]$, $[(s,p)^1P,p]$, $[(p,d)^3P,p]$. For notation see text. Variation of α and β will affect this figure but the essential feature remains the same.

calculation. This, however, does not imply that a Feshbach resonance can be formed at this energy because the ^3P threshold energy is still lower by 0.46 eV. The angular component $[(s,p)^3P,p]$ is not orthogonal to $[(s,p)^1P,p]$ after antisymmetrization. Such a state will decay through the ^3P channel before a resonance state can be formed. Another doubly excited core of interest is the $2p2p\ ^1D$ which is slightly lower than the ^1P target.[19] A 24-term wave function with angular components $[(p,p)^1D,s]$ and $[(d,d)^1D,s]$ gives an energy of -0.7242 a.u. (59.31 eV). For reasons discussed above, it cannot be considered as a resonance.

Since all of the previous theoretical work seems to support the existence of the $^2D(2s2p2p)$ Feshbach resonance, it is appropriate to take a closer look at these calculations. Safranova and Senashenko[13] carried a perturbation theory to the second order, they obtained $-0.793\,572$ a.u. (57.24 eV) for the energy of this state. This energy is about 0.8 eV below the experimental result. It is too far off to give any conclusion about the existence of this Feshbach resonance. In the work of Ahmed and Lipsky,[12] the result is -0.7554 a.u. (58.46 eV). It is above the ^3P threshold energy they have used -0.7576 a.u. (58.40 eV). In this case, the Feshbach resonance cannot be formed for reasons discussed before. The same comment can also be made about the work of Nesbet[14] who gives 58.52 eV. As can be seen from Fig. 1, any energy above this threshold can be obtained variationally as long as ^3P doubly excited core is used. Hence, the state obtained by these authors may not be a $2s2p2p\ ^2D$ Feshbach resonance.

The earliest theoretical calculation on this state is probably done by Eliezer and Pan who used a stabilization method and obtain 58.3 eV. The details of the calculation are not quoted in this reference. However, the authors point out the possibility of a stabilized root which is not a real resonance.[9] Nicolaides[10] calculated the energy of this state and obtained 58.4 eV. Although the details of the calculation are not given in this reference, judging from a private communication between Nicolaides and Schulz[24] the wave function calculated contained 17% $(2s)^2nd$ and $(2p)^2nd$ terms. As discussed before, the inclusion of these terms may lead to erroneous results. Hence, it is not conclusive evidence for the existence of this Feshbach resonance.

Finally, a more elaborate close-coupling calculation was done by Smith *et al.*[11] with four

target states and five channels. The target states are $\phi(1s^2)$, $\phi(1s2s^3S)$, $\phi(1s2s^1S)$, and $\phi(2s2p^3P)$. The ^3P target state wave function used has a threshold energy of 58.36 eV. Since this is the only closed-channel target state used, the closed-channel part of the wave function would be a simple product of this target and the third electron. In spite of this approximation, their calculation gives a resonant structure at 58.34 eV with width 0.0246 eV. The elastic scattering cross section rises just *below* and falls *above* the ^3P threshold. It was pointed out to me[25] that this close-coupling calculation does not distinguish a Feshbach resonance from a threshold effect. In view of the fact that I fail to find this Feshbach resonance with a much more flexible wave function, it is likely that the close-coupling result is showing a threshold effect.

In considering the previous theoretical work in the literature, it appears that a definitive conclusion cannot be made about the nature of the ^2D structure. The present work suggests that it is not a Feshbach resonance. It should be emphasized that the reason is not that I fail to obtain an energy close to the ^2D structure, rather the repulsive nature of the system, i.e., Fig. 1 leads me to believe that a Feshbach resonance cannot be formed. Experimentally, the position of this structure is slightly below the ^3P threshold except the 58.31-eV result by Grissom *et al.*[7] But whether the interaction of the scattered electron with the autoionizing target [6] has slightly lowered the observed ^3P energy hence the experimental finding may actually be a threshold effect is, nevertheless, a possibility. I hope that more work can be done in this area.

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