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Comparison of the saddle-point method and the Feshbach-type projection method

Kwong T. Chung
*Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202**
and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China 10764

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In this work, we compare the saddle-point method with the Feshbach-type projection-operator method using experimental and theoretical data in the literature. It appears that the saddle-point energy gives a better approximation to the resonance energy. This result is explained in terms of the variational principle of quantum mechanics. It is also pointed out that the existing Feshbach-type projection method is not suitable for general triply excited states such as $(2snln'l')$ where $n,n' \geq 3$.

In a recent paper,[1] Bylicki developed a Feshbach-type projection method. He obtained a projection operator for triply excited three-electron systems. His method is particularly interesting in view of the fact that these systems lie above the doubly ionized threshold, and there are an infinite number of open channels associated with these resonances. The traditional Feshbach-type projection-operator method cannot solve these problems easily.[2]

In Ref. 1, for the open-channel space wave function, Bylicki gives

$$P\Psi=(P_1+P_2+P_3-P_1P_2-P_1P_3-P_2P_3+P_1P_2P_3)\Psi\ , \tag{1}$$

where

$$P_i=|\varphi(\mathbf{r}_i)\rangle\langle\varphi(\mathbf{r}_i)|\ . \tag{2}$$

φ is the ground-state wave function of the hydrogenic ion. From Eq. (1), Bylicki obtained the following for the closed-channel wave function:

$$Q\Psi=(1-P)\Psi=\prod_{i=1}^{3}(1-P_i)\Psi\ . \tag{3}$$

Two important features of Eq. (3) have been pointed out by Bylicki. One is that Q is completely symmetric with respect to the electron coordinates. The other is that Eq. (3) takes the same form as the projection operator of the saddle-point method.[3] He also pointed out that the same situation occurs in the case of doubly excited resonances in two-electron systems and states that the successful application of the saddle-point method to triply excited resonances[4] in He^-, Li, and Be^+ justifies the reliability of his approach.

For $(2l2l'2l'')^{2,4}L$ resonances, Eq. (3) does take the same form as the projection operators of the saddle-point method, where projection operators of the form

$$(1-P_{1s})=1-|\varphi_{1s}(q)\rangle\langle\varphi_{1s}(q)|\ , \tag{4a}$$

where

$$\varphi_{1s}(q)=(1/\sqrt{\pi})q^{3/2}e^{-qr} \tag{4b}$$

are used. The only difference is that in the saddle-point method the parameter q is to be optimized rather than taking the hydrogenic value. These two methods are probably among the simplest methods for solving the triply excited three-electron system. With the advance of experimental technique, it is reasonable to expect more and more of these highly excited systems to be found in high-resolution experiments. It is, therefore, important to have a reliable theoretical method to identify the observed spectra.

The saddle-point method is based on the variational principle of quantum mechanics; that is,

$$\delta E=\delta\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{\langle\delta\Psi|H-E|\Psi\rangle+\langle\Psi|H-E|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle}\ , \tag{5}$$

with the trial function covering the proper Hilbert space. To require $\delta E=0$ to be true for arbitrary variation of any and all possible parameters in Ψ, the parameters must be at a value where

$$(H-E)\Psi=0\ . \tag{6}$$

For autoionizing states, the continuum part of the wave function cannot be included in Eq. (5). Therefore, Eq. (6) is only satisfied in the approximate sense.

There are many types of stationary values of E. The saddle-point method suggests that, for those innershell vacancy states with orbital excitation, one can construct the vacancy orbitals with parameters and build these vacancies directly into the wave function. In the variational process, one should maximize the energy with respect to the parameters in the vacancy orbital. This implies that when the same wave function is used, the energy from the saddle-point calculation must necessarily be higher than that from Eq. (3). The question naturally follows: Which result gives a better approximation to the true resonance?

It is difficult to make detailed comparisons from the study of triply excited three-electron systems, because there the experimental data are less precise. There is also the question of the cancellation of errors due to insufficient correlation in the wave function. On the other hand, for two-electron systems, many accurate theoretical and experimental data are available. This is especially true for the helium atom. Here, many high-precision calculations have been carried out.[5] There are also high-precision optical experimental data on helium.[6–8] Some of them are accurate to within 0.01 eV. Hence, in this work, we will use helium to compare the two methods in question.

In the case of helium, the Feshbach-type projection operator of Eq. (3) is identical to the conventional Feshbach projection operator.[9] The shift from the eigenvalue of QHQ to the resonance position is given by

$$\Delta_n^{\mathrm{FT}}(E)=\mathrm{P}\int\frac{|\langle\Phi_n|H|\Psi_\epsilon^+\rangle|^2}{E-\epsilon}d\epsilon\ . \tag{7}$$

That is,

$$E_n^{\mathrm{res}}=E_n^{\mathrm{FT}}+\Delta_n^{\mathrm{FT}}(E_n^{\mathrm{res}})\ . \tag{8}$$

Here E_n^{FT} is the eigenvalue of interest with corresponding eigenfunction Φ_n. Ψ_ϵ^+ is the appropriate continuum wave function.[10] The shift in Eq. (7) is usually referred to as the Feshbach shift. One can also define a shift for the saddle-point method as

$$\Delta_n^{\mathrm{SP}}=E_n^{\mathrm{res}}-E_n^{\mathrm{SP}}=\Delta_n^{\mathrm{FT}}-(E_n^{\mathrm{SP}}-E_n^{\mathrm{FT}})\ , \tag{9}$$

or

$$R=\Delta_n^{\mathrm{SP}}/\Delta_n^{\mathrm{FT}}=1-(E_n^{\mathrm{SP}}-E_n^{\mathrm{FT}})/\Delta_n^{\mathrm{FT}}\ . \tag{10}$$

If R is less than 1, this means that the saddle-point energy lies closer to the resonance energy. But if the ratio is greater than unity, then the Feshbach-type energy is a better approximation.

The Feshbach shifts for helium resonances below the $n=2$ threshold have been calculated by Bhatia and Temkin.[11] Of the 22 resonances calculated for helium, only two states have negative shifts. The Feshbach shifts of the $2s2s\ ^1S$ and $2s2p\ ^1P$ resonances were also calculated by Chung and Davis.[12,13] In Table I, we show this ratio for resonances where the Feshbach shift is significant. For states with very small shifts, both methods should be considered as accurate; they are not included in this table. Perhaps the most remarkable point in this table is that for the two states with negative Δ^{FT}, the saddle-point results should definitely be worse than those of Feshbach. However, we found that for these resonances the q values lie extremely close to $Z=2$, implying that the saddle-point solution and that of the Feshbach method become almost identical.

For resonances in the inelastic region, such as $3s3p\ ^1P$, the operator constructed by Bylicki (Eq. 3) cannot remove the open channels ($2skp$), ($2pks$) or ($2pkd$). Therefore, breakdown will always occur in a variational calculation. It is, however, possible to construct Feshbach-type projection operators for these resonances.[9,15] We can also compare the results from this operator with that from the saddle-point method,[14] as well as with other accurate theoretical[16,17] and experimental[7,8] results. This comparison is given in Table II. Open-channel effects are included in Refs. 16 and 17. Here, we give the results for the lowest $^{3,1}P^\circ$ resonances. The experimental results for the lowest $^1P^\circ$ resonance are highly accurate; the line profile[18] and width are analyzed in great detail. If we assume that the correct resonance position is 69.918 eV, then the saddle-point result is too low by 0.015 eV and, for the Feshbach result, by 0.049 eV. For higher members of the resonance series, as a rule, the differences between the results of the two methods become smaller.

For resonances below the $n=4$ threshold, accurate measurements for $^1P^\circ$ states were obtained by Madden and Codling[6] in 1965. We are not aware of any line-profile analysis for these resonances. For the $4s4p\ ^1P^\circ$ state, the QHQ result with an 85-term wave function is $-0.195\,032$ a.u.[19] The corresponding solution from the saddle-point method is -0.193990 a.u. The energy of the measured line maximum by Madden and Codling is $-0.19271(81)$ a.u.

It is important to understand the mathematical reason why the saddle-point method should give a better result. The wave function of both methods can be symbolically

TABLE I. Comparison of saddle-point method and the Bylicki Feshbach-type projection-operator method for resonance states of helium below the He$^+$ $n=2$ threshold (in a.u.). Square brackets denote powers of 10.

States*	E^{FT}	E^{SP}	$\Delta E=E^{\mathrm{SP}}-E^{\mathrm{FT}}$	q	Δ^{FT}	Half width	R
$^1S(1)$[a]	0.778 761	0.777 882	0.000 879	1.919	0.000 903[b]	0.0023	0.027
$^1S(2)$[a]	0.622 567	0.622 356	0.000 212	2.074	0.000 807[c]	0.000 12	0.737
$^1P(1)$[b]	0.692 775 3	0.692 773 3	0.000 002 0	1.994	−0.000 249[b]	0.000 69	1.008
$^1P(2)$[d]	0.597 091	0.597 078	0.000 013	1.98	0.000 023[c]	0.2[−5]	0.435
$^1P(3)$[d]	0.563 861	0.563 861	0.000 000	2.00	−0.000 074[c]	0.000 18	1.000
$^3P(1)$[d]	0.761 457	0.760 842	0.000 615	1.92	0.001 000[c]	0.000 16	0.385
$^3P(2)$[d]	0.584 888	0.584 822	0.000 066	1.97	0.000 266[c]	0.000 05	0.752
$^1D(1)$[e]	0.702 684	0.702 161	0.000 523	1.753	0.000 893[c]	0.0013	0.414
$^3D(1)$[a]	0.583 790	0.583 774	0.000 016	1.977	0.000 046[c]	0.9[−6]	0.652

[a] Reference 13.

[b] Reference 12.

[c] Reference 11.

[d] Reference 14.

[e] Reference 13. Note that the E^{FT} is printed incorrectly in this reference. The correct result is $-0.702\,684$ a.u.

*The parentheses (x) indicate it is the xth state counted from below.

TABLE II. The ^1P and ^3P autoionizing states of He below the He$^+$ $n=3$ threshold (in eV). 1 a.u. = 27.207 95 eV is used in the conversion.

	Theory				Experiment			
	Burke and Taylor[a]	Ho[b]	E^{FT} [c]	E^{SP} [c]	Dhez and Ederer[d]		Woodruff Samson[e]	
					Energy	$\Gamma/2$	Energy	$\Gamma/2$
^1P	69.917	69.8727±0.0014	69.869	69.903	69.919±0.007	0.066±0.007	69.917±0.012	0.089±0.006
^3P	69.482	69.471±0.0028	69.435	69.461				

[a] Reference 16.

[b] Reference 17.

[c] Reference 14. Energy given in this table is relative to the relativistic ground-state energy of helium at −2.903 800 a.u. as given by Pekeris.

[d] Reference 7.

[e] Reference 8.

written as $O\Psi$, where O represents the operators of the two methods. For the saddle-point method, in general, the antisymmetrization is taken after O has operated on the unsymmetrized wave function. The variation method for $O\Psi$ gives

$$\delta\langle E\rangle=\delta\frac{\langle O\Psi|H|O\Psi\rangle}{\langle O\Psi|O\Psi\rangle}=\frac{\langle\delta O\Psi|H-E|O\Psi\rangle+\langle O\Psi|H-E|\delta O\Psi\rangle}{\langle O\Psi|O\Psi\rangle}\ . \tag{11}$$

Hence, in order to find the best approximation to the Schrödinger equation, the energy E must be stationary with respect to any and all possible parameters in $O\Psi$. In the case of the Feshbach-type projection operator, we have

$$\delta O\Psi=O\delta\Psi\ , \tag{12}$$

since O is fixed. However, for the saddle-point method, we have

$$\delta O\Psi=(\delta O)\Psi+O\delta\Psi\ . \tag{13}$$

That is, more flexibility is allowed in Eq. (11) to better satisfy the Schrödinger equation.

For triply excited three-electron resonances, such as $(2s2s2p)^2P^{\circ}$, the projection operator in Eq. (3) resembles that of the saddle-point method. However, for $(2snln'l')$ resonances with $n,n'\geq 3$, the two methods are completely different. For example, for the $[(2s3s)^1S,3p]^2P^{\circ}$ resonance, the saddle-point method gives, for the two major partial waves $[(0,0)^10,1]$ and $[(1,1)^10,1]$,

$$\begin{aligned}Q\Psi=&\ A[1-P_{1s}(1)][1-P_{1s}(2)][1-P_{2s}(2)]\\&\times[1-P_{2p}(3)]\Phi(r_1,r_2,r_3)[(0,0)^10,1]\\&+A[1-P_{2p}(2)][1-P_{2p}(3)]\\&\quad\times\Phi'(r_1,r_2,r_3)[(1,1)^10,1]\ ,\end{aligned} \tag{14}$$

whereas, Eq. (3) gives

$$\begin{aligned}Q\Psi=&\ [1-P_{1s}(1)][1-P_{1s}(2)][1-P_{1s}(3)]\\&\times A\{\Phi(r_1,r_2,r_3)[(0,0)^10,1]\\&\quad+\Phi'(r_1,r_2,r_3)[(1,1)^10,1]\}\ ,\end{aligned} \tag{15}$$

which is the same equation as one would use to calculate the $(2s2s2p)$ resonance. In the wave function of Eq. (15), all states of the symmetry $(2s2snp)$, $(2s2pns)$, $(2s2pnd)$, and $(2p2pnp)$ will be present. The wave function will also contain the $[(2s2s)^1S,kp]$, $[(2s2p)^{3,1},ks]$, $[(2s2p)^{3,1},kd]$, $[(2p2p)^1S,kp]$, $[(2p2p)^1D,kp]$ and $[(2p2p)^3P,kp]$ continua. Therefore, breakdown cannot be avoided in a variational calculation. It is not clear how one can improve the Q operator in Eq. (15) to overcome the difficulty. This implies that the method of Bylicki cannot be used for general triply excited systems.

In a recent paper,[20] Bylicki remarked that in some situations variational breakdown may occur in a saddle-point calculation. In the case where Eq. (3) is applicable, the method of Bylicki actually guarantees that the saddle-point method will never suffer from variational breakdown. This is because the projection operators in Eq. (3) are fixed, whereas the saddle-point energy is maximized with respect to the parameters in these operators. The saddle-point energy always lies above the energy from Eq. (3).

The situations that Bylicki is concerned about are those resonances, such as $(1s2s2p)^2P^{\circ}$ of He$^-$, that lie between an open-channel with target state $(1s2s)^3S$ and a closed channel with target state $(1s2s)^1S$. In this case, the $2s$ "hole" is not shared by the entire system. As can be seen from Eq. (14) that the construction of the projection operators in a saddle-point calculation is very flexible. There is no reason to forbid the building a certain "hole" in a part of the total wave function in order to remove an open channel. The only criterion is whether the wave function is sound and whether it reflects the physics of the system. The rest is left to the variational principle of quantum mechanics. Reference 3 was criticized for not spelling out explicitly how to prevent variational breakdown for systems like $^2P^{\circ}$ of He$^-$ when an arbitrary wave function is used. Note that $^2P^\circ$ of He$^-$ was considered to be a shape resonance in 1979. The saddle-point method is developed for Feshbach resonances. Nevertheless, it is through the application of the saddle-point method that the Feshbach resonance nature of He$^-$ $^2P^\circ$ is uncovered.[21] In a recent comment,[22] an explicit saddle-point calculation was carried out to show that no variational breakdown will occur in $^2P^\circ$ of He$^-$, even with the wave function of Bylicki. We do not consider this concern of Bylicki to be serious. For example, we refer to the recent work of Jaskolska and Woznicki on $[(1s2s)^1S, nd\,]^2D$ of Li I.[23]

One challenging problem facing the saddle-point method is the high-spin-multiplicity systems consisting of vacancies due to orbital excitation as well as spin symmetry. Recently, we have found an approach to solve this type of problem.[24] Applications have been carried out on ten resonances; very detailed studies have been made. It appears that the results are very satisfactory.[25] We hope that experiments can be carried out to test these predictions in the near future.

The saddle-point method uses projection operators of the form $P_i = 1 - |\varphi_i\rangle\langle\varphi_i|$ to build vacancies into the wave function. This method of building vacancies should be obvious to anyone who is familiar with the Feshbach projection-operator method. In the work of Hahn, O'Malley, and Spruch[26] in 1962, a projection operator is constructed with the product of P_i. It is followed by the many applications of O'Malley and Geltman[9] and Bhatian, Temkin, and Perkins.[27] The projection operator given by Eq. (4) was given in a footnote in Ref. 9. It was also explicitly used by Chen.[28] Note that the form of φ, as well as the total wave function Ψ in the saddle-point method, follows closely that of Ref. 9. The emphasis of the single-particle projection technique in Ref. 3 was on how to determine the projection operator by optimization, rather than by the use of Eq. (4) which is well known in the literature. The most important concept in the saddle-point method is that the "hole" orbital in a physical system is completely different from a "particle" orbital. This is a different approach to the idea of Nicolaides[29] in his Hartree-Fock projection formulation.

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*Present address.

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