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Feshbach-type projection calculations of triply excited resonances in He^-

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The Feshbach-type projection method is applied to the $2s^2 2p\ ^2P^o$ and $2s2p^2\ ^4P^e$ resonances in He^-. The results are compared with the saddle-point technique results and some other calculations by methods closely related to the Feshbach-type projection method.

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I. INTRODUCTION

The Feshbach projection-operator method [1] in its most advanced formulation by Temkin and Bhatia [2] is applicable to doubly excited atomic resonances lying in the inelastic-scattering region with several open channels. The method has been recently extended [3] to the case of an infinite number of open channels associated with all singly excited target states, i.e., to the case of triply excited resonances lying just above the double ionization threshold. The extended method is based on the approximate description of open channel functions as containing the $(N-2)$-electron core represented by the ground-state wave function of doubly ionized system (whose energy level is the double ionization threshold of the N-electron atom).

In this context the three-electron system (He^-) is the simplest but very interesting case where the doubly ionized system is hydrogenic and is described by the one-electron $1s$ function. This function may be interpreted either as the $(N-2)$-electron core in the open-channel space functions, or as the one-electron hole in functions of the closed-channel space. In Ref. [3] the former interpretation was used to define the projector P projecting onto the open-channel space. On the other hand, Nicolaides [4] used the latter interpretation to construct hole-projection operators. In general these techniques are different. However, they are equivalent for three-electron triply excited resonances lying below doubly excited two-electron levels.

The hole-projection operators have also been used by Chung within the saddle-point technique [5,6]. In this method the hole function is optimized so as to maximize the resonant energy. As it has been recently proven [7], this way of optimization follows from the mini-max principle, which demands that the excited-state energy should be maximized with respect to parameters describing an approximate space of lower-lying states. (For further information about the saddle-point technique and its relation to the Feshbach-type approach, see also Refs. [8,9].) The saddle-point technique has been successfully applied to triply excited resonances of three-electron systems [6,10,11]. Since in the three-electron system under consideration the only difference between the saddle-point technique and the Feshbach-type method is the above-mentioned maximization, the question arises how large the effect of this maximization is, i.e., whether the Feshbach-type projection method can provide as good results as those of the saddle-point method.

In order to answer this question, which is the main aim of this work, I have performed calculations by both methods within the same basis sets. These calculations have been carried out for the $2s^2 2p\ ^2P^0$ and $2s2p^2\ ^4P^e$ resonances of He^-. The $2s^2 2p\ ^2P^0$ resonance was discovered by Kuyatt, Simpson, and Mielczarek [12] and interpreted as such by Fano and Cooper [13]. It was confirmed by other experimental [14–18] and theoretical [6,19–22] works. The present results are in good agreement with the experimental data. The $2s2p^2\ ^4P^e$ resonance has not yet been observed but it was predicted by Chung [11] and Chung and Davis [6].

II. FESHBACH-TYPE PROJECTION METHOD FOR TRIPLY EXCITED RESONANCES

The Feshbach-type projection method for triply excited resonances [3] shall be presented here in a specific formulation of a three-electron atom. Let us assume that the lowest triply excited resonant levels lie above the double ionization threshold, i.e., above the ground-state level of a hydrogenic ion, but below doubly excited two-electron thresholds. The method is based on the assumption that each open-channel function can be written as

$$\Phi=\mathcal{A}\phi(\mathbf{r}_1)u(x_2,x_3,1)\ , \tag{1}$$

where $\mathcal{A}$ is the three-electron antisymmetrizer, $\phi(\mathbf{r}_1)$ is the spatial part of the hydrogenic ground-state wave function (one-electron core), and $u(x_2,x_3,1)$ is a function of the proper total angular momentum of the two remaining electrons, coupled to the spin part of the core to form the proper spin of the entire system. The spin coordinate of the core electron is denoted by 1.

The projection operators P and Q projecting, respectively, onto the open-channel space and its orthogonal complement must fulfill the following conditions:

$$P\Psi=\mathcal{A}\phi(\mathbf{r}_1)u(x_2,x_3,1) \tag{2}$$

for an arbitrary antisymmetric three-electron function Ψ, and

$$P+Q=\mathbb{1},\quad PQ=0,\quad P^\dagger=P\ . \tag{3}$$

These conditions lead to a strong orthogonality requirement

$$\langle\phi(\mathbf{r}_1)|(1-P)\Psi\rangle=0\ . \tag{4}$$

The question how to realize projection onto P or Q space can be answered by solving a set of Eqs. (2) and (4). There are two ways of doing this. One of them, described in detail in Ref. [3], gives explicit forms of operators P and Q which read

$$P=P_1+P_2+P_3-P_1P_2-P_1P_3-P_2P_3+P_1P_2P_3 \quad (5)$$

and

$$Q\equiv \mathbb{1}-P=\prod_{i=1}^{3}(1-P_i) , \quad (6)$$

where

$$P_i\equiv|\phi(\mathbf{r}_i)\rangle\langle\phi(\mathbf{r}_i)| . \quad (7)$$

Thus, in order to obtain $Q\Psi$ one should act on Ψ with the operator Q as defined in Eqs. (6) and (7). This procedure is well known as the hole-projection technique [6]. Although it was derived from assumptions (2) and (3) in Ref. [3], it was earlier derived in another way and applied by Nicolaides [4] and was used by Chung within his saddle-point method [6]. A procedure equivalent to the hole-projection one was also used by Ahmed and Lipsky [21].

The other way of solving Eqs. (2) and (4) is to find $P\Psi$ for a given Ψ, i.e., to find an appropriate u which is necessary to form $P\Psi$ according to Eq. (2). Assuming that the trial function Ψ is of configuration expansion form and considering the form of $P\Psi$ obtained by using Eq. (5), one finds out that u is strictly expressible in terms of ϕ and orbitals appearing in Ψ. Thus one can easily forecast a finite (but strict) expansion form for u. Coefficients of this expansion can be found from a set of linear algebraic equations obtained from Eq. (4). (In Ref. [3] this procedure is described in detail for a general N-electron case.) When $P\Psi$ is obtained in this way, then $Q\Psi=(1-P)\Psi$ is also known.

In the case under consideration (triply excited 3-electron resonances lying above the double ionization threshold but below doubly excited two-electron levels) this procedure is equivalent to the hole-projection technique provided the trial function Ψ is of configuration expansion form. This is not a weighty limitation because trial functions of that type are mostly being used in actual calculations. On the other hand, the algorithm mentioned above holds for the more general case, i.e., for resonances lying in an arbitrary energetic region. Therefore this algorithm has been applied in the computer code I used in my calculations.

Feshbach projection, regardless of the way in which it is realized, can be used in calculations in which the Rayleigh-Ritz variational method is applied to the QHQ operator, where H is the nonrelativistic Hamiltonian of a three-electron atom. The QHQ-matrix eigenvalues lying below the doubly excited two-electron levels are interpreted as energies of triply excited resonances. Such calculations will be referred to as QHQ calculations.

III. CALCULATIONS, RESULTS, AND DISCUSSION

The method described above can be applied, without modifications, to resonances lying just above the He^+ ground state but below the next threshold, which is the $2s^2\,{}^1S$ resonance of He. (For resonances lying above the $2s^2$ threshold, the open channel $2s^2kl$ should also be projected out from the Q space, etc.) The $2s^22p\,{}^2P^0$ and $2s2p^2\,{}^4P^e$ resonances are the only two lying below the $2s^2$ level of He. Since both of them have been calculated by Chung [10,11] and Chung and Davis [6] by means of the saddle-point technique, the basis-set experience of these authors has been taken into account in this work. Most of the spin-angular terms used by Chung and Davis [6] have been included in the present calculations with nonlinear parameters optimized by them. This was possible because Slater-type orbitals have been used both in this work and in the calculations of Chung and Davis [6]. Nevertheless, the basis sets used in this work are not the same as those of Ref. [6], since the radial terms have

TABLE I. $2s^22p\,{}^2P^0$ resonance energy calculation.

Spin-angular terms	Number of radial terms	Nonlinear parameters			$-\Delta E$ (a.u.)	
					QHQ	Saddle point[a]
$(s,s)\,{}^1S,p$	34	0.74	0.74	0.725	0.753 468	0.753 392
$(p,p)\,{}^1S,p$	15	0.8	0.8	0.7	0.027 835	0.027 250
$(s,p)\,{}^3P,d$	18	0.72	0.81	0.8	0.008 530	0.008 419
$(s,p)\,{}^1P,d$	18	0.47	0.71	0.9	0.006 531	0.006 506
$(p,d)\,{}^1P,d$	9	0.63	0.99	0.65	0.002 565	0.002 543
$(s,p)\,{}^1P,s$	19	0.36	0.72	0.85	0.001 076	0.001 034
$(p,p)\,{}^1D,f$	5	0.84	0.84	1.05	0.000 484	0.000 479
$(s,d)\,{}^1D,f$	4	0.59	0.85	1.2	0.000 568	0.000 561
$(p,d)\,{}^3P,d$	7	0.75	0.75	0.75	0.000 153	0.000 151
$(p,d)\,{}^1P,s$	8	0.72	0.72	0.9	0.000 096	0.000 075
$(s,p)\,{}^3P,s$	19	0.36	0.72	0.85	0.000 075	0.000 082
$(d,d)\,{}^1S,p$	8	1.2	1.2	0.7	0.000 072	0.000 074
$(p,p)\,{}^3S,p$	5	0.8	0.8	0.7	0.000 054	0.000 053
$(p,d)\,{}^1P,d$	2	0.75	0.75	0.75	0.000 035	0.000 034
$(s,d)\,{}^3D,f$	4	0.47	1.05	1.4	0.000 012	0.000 011
Total	175				0.801 554	0.800 664

[a] The optimal q is 1.91.

been chosen independently. In order to systematically compare results of the *QHQ* and saddle-point methods, I performed both the saddle-point and *QHQ* calculations using the same basis sets. The radial part of function $\phi(\mathbf{r})$, in terms of which the operator Q is defined in Eqs. (6) and (7), was $R_{1s}(r)=Ce^{-qr}$, where C is the normalization factor and q was 2.0 for the *QHQ* calculation; q was instead optimized in the saddle-point calculation to maximize the resonance energy.

The results are displayed in Tables I and II. The spin-angular terms are ordered in these tables with respect to the magnitude of their contributions ($-\Delta E$) to the resonant energy. The fact that the $[(s,d)^1D,f]$ spin-angular term, appearing in Table I after the $[(p,p)^1D,f]$ term, has a greater contribution than the latter, is due to the strong interaction between them. As one can see, the spin-angular term sequence has turned out to be the same for the saddle-point and *QHQ* calculations (except that the order of the $[(p,d)^1P,s]$ and $[(s,p)^3P,s]$ terms has been changed in the saddle-point calculation, see Table I). The quantitative differences between the saddle-point and the *QHQ* results are exclusively due to the maximization of the energy with respect to q. These differences are about 0.025 eV for both states. Very recently Chung [23] performed more-accurate *QHQ* and saddle-point calculations (in a basis set of 302 functions) for the $2s^22p\ ^2P$ resonance. His results are, respectively, $-0.801\,974$ and $-0.801\,125$ a.u. They differ between each other by about 0.023 eV. Thus, the differences between the *QHQ* and saddle-point results for the resonances under consideration are of the same magnitude as the corresponding differences in the case of the lowest $^1S^e$ resonance of He, where the relation between the Feshbach projection and the hole projection is the same as in our case [6].

Comparison of theoretical and experimental position of $2s^22p\ ^2P$ is given in Table III. As one can easily see, the *QHQ* results match the experimental data best. Chung's saddle-point result is the best among the saddle-point data. It is the lowest one just because of the better choice of basis set; the maximization has been performed in all the saddle-point calculations with respect to the same representation of the 1s hole.

It is very interesting to compare the *QHQ* results with those of Ahmed and Lipsky [21] and Nicolaides [4]. Ahmed and Lipsky [21] used the hydrogenic wave functions, with the 1s orbital omitted, as a one-electron basis set. Within this basis they obtained multiconfigurational wave functions of some lower-lying doubly excited He states. Then they multiplied them by hydrogenic orbitals (still except 1s) describing the third electron and diagonalized the Hamiltonian matrix obtained in this basis set. This gave the position of $^2P^0$ at 57.350 eV above the He ground-state level. In Table III this method is referred to as the closed-channel expansion. Another Ahmed and Lipsky result, of 57.305 eV was obtained using the straightforward configuration-interaction expansion (within the same orbital basis set) for the resonant wave function. After completing this calculation, performed as a numerical experiment, they modestly suggested that orthogonality to the 1s orbital is all that is necessary to define triply excited states, and that a projection operator can be constructed which projects out the ground state of a one-electron system. Such a projector is defined in Eq. (6) and was in fact used before by Nicolaides [4]. Thus, calculations of Nicolaides [4] and Ahmed and Lipsky [21] are equivalent to the *QHQ* calculations [25] and therefore marked in Table III as "*QHQ*." The best $2s^22p$ resonance position obtained in the *QHQ* calculation by Chung [23] at 57.192 eV is lower, i.e., better, than the "*QHQ*" results only because of the better choice of variational manifold.

The existence of $2s2p^2\,{}^4P^e$ resonance in He$^-$ was predicted by Chung [11]. Its position obtained by Chung and Davis [6] is 57.421 eV above the helium ground state. The position obtained in this work is 57.420 eV in the case of the saddle-point calculation or 57.395 eV in the *QHQ* calculation. This resonance cannot be observed in the experiment in which the electron is scattered from the He ground state, but it is hoped that it will be observed in other experiments in the future and that the theoretical predictions will be confirmed.

The *QHQ* results, as well as those obtained in this work and that of Chung, do not differ very much from those obtained by means of the saddle-point technique. The case of the $2s^22p$ resonance suggests that they can be in even better agreement with experimental data than the latter. It cannot be stated, however, which of those two methods is better, because a coupling to the continuum shift, which could be of both signs, is not included in the calculations presented here. Nevertheless, the fact that the results of the Feshbach-type projection method and the saddle-point technique are close to each other and

TABLE II. $2s2p^2\,{}^4P^e$ resonance energy calculation.

Spin-angular terms	Number of radial terms	Nonlinear parameters			$-\Delta E$ (a.u.) *QHQ*	$-\Delta E$ (a.u.) Saddle point$^{\mathrm{a}}$
$(s,p)\,^3P,p$	29	0.75	0.66	0.775	0.784 872	0.784 052
$(s,d)\,^3D,d$	13	0.6	1.05	0.9	0.004 240	0.004 245
$(p,d)\,^3P,p$	8	0.72	0.91	0.725	0.003 977	0.003 899
$(p,f)\,^3D,d$	4	0.75	1.05	0.8	0.000 543	0.000 540
$(p,p)\,^3P,d$	9	0.78	0.78	0.75	0.000 464	0.000 475
$(s,f)\,^3F,f$	5	0.59	1.35	1.1	0.000 231	0.000 231
$(d,f)\,^3P,p$	7	0.91	1.1	0.675	0.000 176	0.000 173
Total	75				0.794 503	0.793 615

$^{\mathrm{a}}$The optimal q is 1.885.

TABLE III. Position of the $2s^22p\ ^2P^0$ resonance in He$^-$, calculated relative to the He ground-state level, which is $-2.903\,724$ a.u. (Ref. [24]).

Reference	Method	E (eV)
Theoretical		
Eliezer and Pan (Ref. [19])	Stabilization	57.3
Nicolaides (Ref. [4])	"QHQ"[a]	57.3
Smith *et al.* (Ref. [20])	Close coupling	57.48
Ahmed and Lipsky (Ref. [21])	Closed-channel expansion	57.350
	"QHQ"[a]	57.305
Safronova and Senashenko (Ref. [22])	Second-order perturbation	56.75
Chung and Davis (Ref. [6])	Saddle point	57.225
Present work	Saddle point[b]	57.228
	QHQ[b]	57.204
Chung (Ref. [23])	Saddle point[b]	57.215
	QHQ[b]	57.192
Experimental		
Kuyatt, Simpson, and Mielczarek (Ref. [12])		57.1±0.1
Grissom, Compton, and Garret (Ref. [14])		57.21±0.06
Quemener, Pacquet, and Marmet (Ref. [15])		57.15±0.04
Sanche and Schulz (Ref. [16])		57.16±0.05
Hicks *et al.* (Ref. [17])		57.22±0.04
Roy, Delâge, and Carette (Ref. [18])		57.19±0.03

[a] See discussion in the text.
[b] a.u. $=27.211\,65$ eV.

that they agree quite well with the available experimental data shows that the description of the open-channel space as given in Eq. (1), which in the case under consideration is fundamental for both methods, works well. The hole-projection methods, i.e., the Nicolaides method and the saddle-point technique of Chung, have been successfully applied to atoms with more than three electrons [4,26]. Keeping in mind that the Feshbach-type projection method allows implementation of a better description of the $(N-2)$-electron core in the open-channel space representation than is possible within the saddle-point method [27], we believe that the Feshbach-type projection method is capable of providing good results also for systems with atoms of more than three electrons.

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