Theoretical study of the ^1P doubly excited autoionization state of the magnesium atom

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We present a theoretical study of the $3pns$ and $3pnd$ ^1P doubly excited autoionization series above the first-ionization threshold of magnesium atom. The effect of the configuration interaction on the width and the energy position of the autoionization state is examined in detail. In particular, we have shown that the width of the narrow $3pnd$ ^1P series is strongly affected by the configuration interaction. The results of the present calculation are also in good agreement with the existing theoretical and experimental data. In addition, the present theoretical approach is shown to be effective in the quantitative calculation for higher excited states in the autoionization series.

I. INTRODUCTION

In a recent paper[1] (hereafter referred to as I), we have demonstrated that the two-electron interaction between the two outer electrons of an alkaline-earth atom is well represented by a nonlocal interaction potential. A simple application of this approach to the Mg atom has led to a good agreement between the experimental and the calculated energy values of the doubly excited $3pns$ and $3pnd$ ^1P configuration series. As we pointed out in I, a more comprehensive study of the doubly excited autoionization state should also include the interaction between the doubly excited bound state and the open background channel which includes both discrete $3snp$ and continuum $3s\epsilon p$ configurations. In this paper, we will examine in detail the effect of this interaction on the width and the corresponding energy shift of the autoionization state. In particular, we will show that no additional numerical effort is required to reach convergence for the highly excited states in the autoionization series. Studies of these higher excited states have also attracted considerable interest in the recent multistep laser experiments.[2]

II. THEORETICAL PROCEDURE

The theoretical procedure employed in this study is similar to that developed by Fano[3] and Bates and Altick.[4] The state function of the doubly excited autoionization state is given by

$$\Psi_E=\sum_{nl} f_{nl}(E)\Phi_{nl}+\sum_{np} a_{np}(E)\Psi_{3snp}+\int d\epsilon\, a_{\epsilon p}(E)\Psi_{3s\epsilon p}\ , \tag{1}$$

where Φ_{nl} is a multiconfiguration state wave function representing a doubly excited state dominated by a single configuration $3pnl$ (e.g., $nl=ns$ or nd) as given by Eq. (12) of I. The configuration wave function Ψ for the individual open-channel configuration $3snp$ or $3s\epsilon p$ is defined by Eq. (3) of I. The expansion coefficients f_{nl} and $a_{n(\epsilon)p}$ are functions of energy E. Following the treatment of I, the matrix elements of the N-particle nonrelativistic Hamiltonian are

$$\langle\Phi_{nl}\,|\,\hat{H}\,|\,\Phi_{n'l'}\rangle=\delta_{nn'}\delta_{ll'}E_{3pnl}\ , \tag{2a}$$

$$\langle\Phi_{nl}\,|\,\hat{H}\,|\,\Psi_{3sv(\epsilon)p}\rangle=V_{nl,v(\epsilon)p}\ , \tag{2b}$$

$$\langle\Psi_{3snp}\,|\,\hat{H}\,|\,\Psi_{3sn'p}\rangle=\delta_{nn'}(\epsilon_{3s}+\epsilon_{np})\ , \tag{2c}$$

$$\langle\Psi_{3snp}\,|\,\hat{H}\,|\,\Psi_{3s\epsilon p}\rangle=0\ , \tag{2d}$$

$$\langle\Psi_{3s\epsilon p}\,|\,\hat{H}\,|\,\Psi_{3s\epsilon' p}\rangle=\delta(\epsilon-\epsilon')(\epsilon_{3s}+k^2)\ . \tag{2e}$$

One of the main differences between the present approach and that of Bates and Altick[4] is that the Hamiltonian is already diagonal with respect to the doubly excited discrete state wave functions Φ_{nl} in the present treatment as shown by Eq. (2a). The energy of the electron in the continuum is $\epsilon=k^2$ in Rydberg units. The orbital energy is calculated by solving Eqs. (9) and (10) of I.

Parallel to the derivation of Fano,[3] the equation for the expansion coefficient f_{nl} takes the form

$$\sum_{n'l'} U_{nl,n'l'}(E)f_{n'l'}(E)+z(E)\sum_{n'l'} W_{nl,n'l'}(E)f_{n'l'}(E) =(E-E_{3pnl})f_{nl}(E)\ , \tag{3}$$

where U is the second-order contribution to the interaction energy between the discrete states $3pnl$ and the entire open channel $3sn(\epsilon)p$, i.e.,

$$U_{nl,n'l'}(E)=\sum_{vp}\frac{V_{nl,vp}V_{vp,n'l'}}{E-(\epsilon_{3s}+\epsilon_{np})}+\int d\epsilon\frac{V_{nl,\epsilon p}V_{\epsilon p,n'l'}}{E-(\epsilon_{3s}+\epsilon)}\ , \tag{4}$$

and W is a measure of the strength of the configuration interaction given by

$$W_{nl,n'l'}(E)=\left[\frac{1}{\pi k_0}\right]V_{nl,\epsilon_0 p}V_{\epsilon_0 p,n'l'}\ , \tag{5}$$

where $\epsilon_0=E-\epsilon_{3s}$ and the factor πk_0 is included so that the radial wave function $\chi_{\epsilon p}$ is normalized according to the asymptotic expression

$$\chi_{\epsilon l}\underset{r\to\infty}{\longrightarrow}\sin[kr+(1/k)\ln(2kr)-\tfrac{1}{2}l\pi+\delta_l]\ . \tag{6}$$

The function $z(E)$ is related to the phase shift Δ due to

the configuration interaction of ψ_E with the state Φ_{nl},[3] i.e.,

$$\Delta(E) = -\tan^{-1}[\pi/z(E)] \ . \tag{7}$$

To calculate $z(E)$, we first diagonalize a matrix U' defined by

$$U'_{nl,n'l'}(E) = U_{nl,n'l'}(E) + \delta_{nn'}\delta_{ll'}E_{3pnl} \ . \tag{8}$$

A straightforward derivation similar to the approach of Fano[3] leads to the expression

$$z(E) = \pi \left[\sum_{\mu} \frac{|V'_{\epsilon_0\mu}|^2}{E - \epsilon_\mu(E)} \right]^{-1} , \tag{9}$$

where ϵ_μ is the energy eigenvalue obtained in the diagonalization of U' and

$$V'_{\epsilon_0\mu}(E) = \sum_{nl} k_0^{-1/2} V_{nl,\epsilon_0 p} A_{\mu,nl}(E) \ . \tag{10}$$

$A_{\mu,nl}$ is the unitary matrix which diagonalizes the matrix U'. Finally, we calculate the width Γ_μ and the resonance energy E_μ of the autoionization state μ by fitting the phase shift $\Delta(E)$ to the equation[4,5]

$$\Delta(E) = \alpha E^2 + \beta E + \gamma + \sum_{\mu} \tan^{-1}[\tfrac{1}{2}\Gamma_\mu/(E_\mu - E)] \ . \tag{11}$$

The other important difference between the present calculation and that of Bates and Altick[4] is in the numerical procedure for the matrix $U_{nl,n'l'}$. Instead of replacing the integration of ϵ with a finite sum over a selected number of chosen energies as done by Altick and Moore,[6] the principal-value integral in Eq. (4) is evaluated exactly in a numerical procedure using the differential equation method we developed earlier.[7] This procedure not only leads to a more accurate numerical result but also reduces the numerical effort substantially.

III. RESULTS AND DISCUSSION

In order to compare with the experimental result, we have included the contribution from the core-polarization effect in our energy calculation as we did in paper I. Again, the energy level of the ground state of the Mg III ion is set equal to zero. Table I lists the result of the calculated energy for the $3pnl\ ^1P$ autoionization series. Column A represents the values of the resonance energy including the energy shift due to the interaction between the doubly excited discrete states $3pnl$ and the open channel $3sn(\epsilon)p$ after a least-squares fit of the phase shifts Δ to Eq. (11). This result is compared with the calculated energies corresponding to the multiconfiguration state Φ_{nl} (column B) and the single-configuration result (column C) from I. It is evident that the energy difference between the more elaborate calculation and the single configuration calculation is small for all higher excited states. This supports our earlier conclusion that the dominant two-electron interaction is indeed included in the interaction potential we introduced in paper I. We also note that the shift due to the configuration interaction between $3pnl$ and $3sn(\epsilon)p$ is larger for the $3pnd$ series than that for the

TABLE I. The calculated energy values for the $3pns$ and $3pnd\ ^1P$ autoionization series of Mg atom. Column A gives the final result of the present calculation. Columns B and C are results corresponding to the multiconfiguration and single-configuration calculations from I. All energies are relative to the ground state of Mg III in Rydberg units.

State	A	B	C
$3p4s$	−0.957 38	−0.958 98	−0.946 27
$3p5s$	−0.866 00	−0.865 60	−0.862 81
$3p6s$	−0.830 87	−0.830 60	−0.829 54
$3p7s$	−0.813 58	−0.813 41	−0.812 87
$3p8s$	−0.803 77	−0.803 65	−0.803 33
$3p9s$	−0.797 60	−0.797 52	−0.797 37
$3p3d$	−0.881 58	−0.886 54	−0.878 95
$3p4d$	−0.838 25	−0.840 14	−0.837 11
$3p5d$	−0.817 62	−0.818 52	−0.817 01
$3p6d$	−0.806 19	−0.806 68	−0.805 83
$3p7d$	−0.799 20	−0.799 49	−0.798 99
$3p8d$	−0.794 61	−0.794 80	−0.794 50

TABLE II. Excitation energy of the ^1P autoionization state in eV measured from the ground state of Mg.

	Experiment		Theory				
State	Ref. 8	Ref. 9	Present	Ref. 1	Ref. 11	Ref. 10	Ref. 4
$3p4s$	9.752	9.76	9.655	9.633	9.706	9.62	10.0
$3p5s$	10.917	10.95	10.898	10.904	10.91	10.90	11.1
$3p6s$	11.385		11.376	11.380	11.38	11.38	11.5
$3p7s$	11.614		11.611	11.614	11.62	11.60	
$3p8s$	11.749		11.745	11.747			
$3p9s$	11.832		11.829	11.830			
$3p3d$	10.653	10.69	10.686	10.619	10.66	10.61	10.8
$3p4d$	11.254		11.276	11.250	11.25	11.25	11.4
$3p5d$	11.549		11.556	11.544	11.55		
$3p6d$	11.706		11.712	11.705	11.71		
$3p7d$	11.806		11.807	11.803			
$3p8d$	11.869		11.870	11.867			

TABLE III. The width of the ^1P autoionization series of Mg and a.u. All values should be multiplied by the powers of 10 indicated by the figure in square brackets.

State	Γ	$\Gamma^{(2)}$	$\Gamma^{(1)}$	Ref. 4	Ref. 13
$3p4s$	1.96[−2]	1.72[−2]	1.97[−2]	1.58[−2]	1.58[−2]
$3p5s$	4.66[−3]	4.25[−3]	6.55[−3]	4.90[−3]	4.5[−3]
$3p6s$	1.84[−3]	1.74[−3]	2.96[−3]	2.23[−3]	
$3p7s$	9.90[−4]	8.78[−4]	1.59[−3]		
$3p8s$	5.12[−4]	5.06[−4]	9.52[−4]		
$3p9s$	3.10[−4]	3.13[−4]	6.15[−4]		
$3p3d$	6.16[−5]	2.94[−5]	1.64[−4]	1.5[−4]	1.8[−4]
$3p4d$	7.25[−6]	5.51[−8]	9.14[−5]	7.5[−5]	
$3p5d$	2.36[−7]	1.88[−6]	5.25[−5]		
$3p6d$	4.23[−7]	4.01[−6]	3.23[−5]		
$3p7d$	1.59[−6]	5.08[−6]	2.11[−5]		
$3p8d$	2.88[−6]	5.74[−6]	1.45[−5]		

$3pns$ series. This is caused partly by the substantial cancellation between the large contributions from the continuum background (i.e., broad autoionization width) from both sides of the resonance energy to the principal value integral $U_{nl,nl}$ for the ns series. On the other hand, for the $3pnd$ series, due to the very narrow autoionization width of the $3pnd$ states, very little contribution to the $U_{nl,nl}$ comes from the continuum and consequently the main correction results from the combined strength from the entire series of discrete $3snp$ configurations.

Table II compares the result of the present calculation (column A) for the excitation energy in eV with the available experimental data[8,9] and other earlier calculations.[1,4,10,11] We note that the result of our previous calculation,[1] which excludes the interaction between the doubly excited discrete configuration and the $3s\epsilon(n)p$ open channel, is in close agreement with a similar model potential calculation by Laughlin and Victor.[10] The result of Bates and Altick[4] should be in closer agreement with the present result than it appears to be if the correction due to the core-polarization effect were taken into account. Our result is also in close agreement with the more elaborate scattering calculation.[11] The small discrepancy between the theory and experiment may have been caused by the nearby minimum in the cross section above the first-ionization threshold[9,12] which could tilt the experimental peak slightly to the higher energy side for the $3p4s$ state.

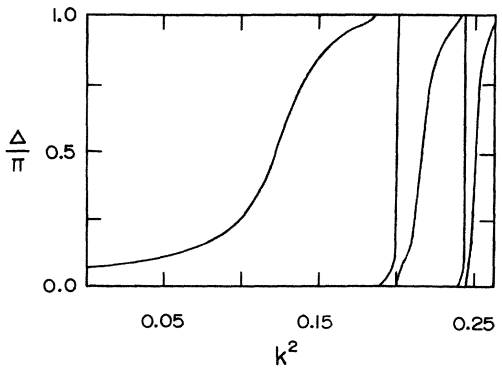

FIG. 1. The calculated phase shift Δ as function of k^2 (Rydberg units).

To examine the effect of the configuration interaction in wave function to the width of the autoionization states, we first estimate the "zeroth-order" width

$$\Gamma_{nl}^{(1)}=2\pi\,|\,\langle\Psi_{3s\epsilon_0 p}\,|\,\hat{H}\,|\,\Psi_{3pnl}\rangle\,|^2/(\pi k_0) \tag{12}$$

with the single-configuration wave function Ψ_{3pnl}. Our next step is to calculate the "multiconfiguration width" $\Gamma^{(2)}$ by replacing Ψ_{3pnl} with the multiconfiguration state wave function Φ_{nl} in Eq. (12). Finally, we determine the width Γ_μ by a least-squares fit of the phase shift $\Delta(E)$ to Eq. (11). In the present calculation, the fitted Δ differs from the input Δ in the last iteration of the least-squares-fit procedure by an amount less than 0.01% and the background contribution, i.e., $\alpha E^2+\beta E+\gamma$ in Eq. (11), is smooth throughout the entire energy region. A portion of the phase shift $\Delta(E)$ is shown in Fig. 1.

Table III compares the width Γ in a.u., calculated from Eq. (11), to $\Gamma^{(1)}$ and $\Gamma^{(2)}$. It is evident that the width is strongly affected by the configuration interaction. In particular, we note a reduction of two orders of magnitude of the width in the $3pnd$ series. The minimum in width between $3p4d$ and $3p7d$ states is caused by a change of sign in the interaction matrix $V_{nl,\epsilon_0 p}$ as E increases. Such a narrow width would correspond to a state of life time of order of one-tenth of a picosecond. For the "broad" $3pns$ series, the reduction from the single configuration width $\Gamma^{(1)}$ is significant although it is not as drastic as that for the narrow $3pnd$ series.

The width determined in other previous calculations[4,13] are also listed for comparison. The experimental determination of the widths is not definitive. We have estimated the widths from the most recent photoionization experiment[9] for the $3p4s$ and $3p5s$ to have values in the neighborhood of 0.48 eV and 0.125 eV (i.e., 0.0176 and 4.59×10^{-3} a.u.), respectively. We can only conclude that the experiment and theory are in fair agreement. A more conclusive measurement would provide a more critical test to the theory. The result of the present calculation is also in qualitative agreement with a recent eigenchannel R-matrix study by O'Mahony and Greene.[14]

Finally, we should point out that in the numerical calculation for the higher states of the autoionization series, very little additional effort is required as the dominant two-electron interaction is already included in the potential proposed in I. All calculations presented in this paper were carried out on a tabletop personal computer.

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