

Effect of the configuration interaction on the  $(3snl)^1L$  bound states of the magnesium atom

T. N. Chang

*Physics Department, University of Southern California, Los Angeles, California 90089-0484*

(Received 7 July 1986)

We present the result of a simple superposition of configuration calculation of the term values for the  $^1S$ ,  $^1P$ , and  $^1D$  singly excited states of the Mg atom. In particular, we have examined quantitatively the importance of the configuration interaction between the doubly excited perturber and the singly excited  $3snl$  series. The numerical result of this calculation is in excellent agreement with the experimental data, including the highly excited states.

## I. INTRODUCTION

Recent interests in the study of the multistep laser processes<sup>1</sup> have led to the need for a simple yet quantitatively effective theoretical approach for the highly excited states of the alkaline-earth-metal atoms. At energy below the first ionization threshold, most of the existing theoretical methods<sup>2-8</sup> are capable of dealing with the strong interaction between the doubly excited "perturber" and the entire singly excited configuration series.<sup>9</sup> One of the most extensively used theoretical approaches is the configuration-interaction method.<sup>2-5</sup> Its applications have led to considerable success in the energy calculation for the ground state and the lower excited states. The scattering approach with model potential developed by Norcross and Seaton<sup>6-7</sup> has also been applied successfully. Straightforward extension of these existing methods to highly excited states would often require substantial numerical efforts.

It is the purpose of this paper to demonstrate that, with minor modification to the nonlocal interaction potential

presented in a recent paper,<sup>10</sup> the simple method of the superposition of configuration wave function approach can be applied with high accuracy to the highly excited states with little additional numerical effort. More specifically, we will present the application of this approach to the determination of the term values of the  $^1S$ ,  $^1P$ , and  $^1D$  singly excited states of a Mg atom below the first ionization threshold. The contribution of the configuration mixing from the doubly excited perturber to the term values will also be examined in detail.

## II. THEORETICAL PROCEDURE

In this section we briefly summarize the theoretical procedure used in the present calculation. A more detailed description of this approach is outlined in our earlier paper<sup>10</sup> (hereafter referred to as paper I).

For each two-electron configuration  $(n_i l_i, n_j l_j)$  pertaining to given total spin  $S$  and total orbital angular momentum  $L$ , a configuration wave function is given by

$$\Psi_{n_i l_i, n_j l_j}^{SL} = \sum_{\text{all } m_i m_j} (-1)^{l_i - l_j} [(2S+1)(2L+1)]^{1/2} \begin{pmatrix} l_i & l_j & L \\ m_i & m_j & M \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ m_{s_i} & m_{s_j} & M_s \end{pmatrix} \phi_{n_i l_i, n_j l_j}^{m_i m_{s_i} m_j m_{s_j}}, \quad (1)$$

where

$$\phi_{n_i l_i, n_j l_j}^{m_i m_{s_i} m_j m_{s_j}}(\mathbf{r}_1, \dots, \mathbf{r}_N) = (N!)^{-1/2} \text{Det}_N | u_\alpha(\mathbf{r}_\mu) | \quad (2)$$

is the Slater determinant wave function consisting of  $N$  one-particle electronic orbital wave functions, i.e.,

$$u_\alpha(\mathbf{r}_\mu) = \chi_{n_\alpha l_\alpha}(r_\mu) Y_{l_\alpha m_\alpha}(\Omega_\mu) \sigma_{m_{s_\alpha}}. \quad (3)$$

The radial part of the one-particle orbital wave function, i.e.,  $\chi$ , is generated with the nonlocal interaction potential given by Eqs. (9)–(11) of I. With this choice of potential it was shown in I that the Hamiltonian matrix is diagonal with respect to the configuration series  $3snl$ .

To calculate the energy eigenvalues, we diagonalize the Hamiltonian matrix constructed with the configuration wave functions  $\Psi$  by including as many contributing configurations as necessary for given  $S$  and  $L$ . The state

wave function  $\Phi$  for each state is then constructed by the simple superposition of the configuration wave functions. We have also included in the Hamiltonian matrix the energy contribution due to the core dipole polarization and the dielectronic potential of Bottcher and Dalgarno<sup>11</sup> with a procedure similar to the one outlined in I. For the  $3snl$  singlet series, the cutoff radius  $r_0 = 1.011a_0$  is used to fit the experimentally observed  $3s$  ionization threshold.

For the highly excited states in the  $3sns^1S$  and  $3snp^1P$  series, the  $n$  dependence of the observed quantum defects is very small. Therefore, by using the interaction-potential approach, we expect that the individual state can be represented adequately by a single dominating configuration as we have demonstrated in paper I for the  $3pnl^1P$  doubly excited series. On the other hand, for the ground state and the lower excited states, it is known that the configuration mixing is very strong. Since the interaction

potential we have proposed has the effect of condensing the two-electron interaction, it tends to underestimate the configuration mixing with the strong interacting doubly excited perturber. To remove this difficulty, we have used the simple *Hartree-Fock radial wave function* [i.e., use of Eq. (7) and (9) in I] for the  $3s^2$  and the  $3s3p$  configurations in the present calculation. For the  $3snd\ ^1D$  series, the  $n$  dependence of the quantum defect is very strong even for the highly excited states due to the large mixing with the  $3p^2$  configuration in the vicinity of the  $3s$  ionization threshold. Consequently, we do not expect that the individual state could be represented by a single configuration, and the simple *Hartree-Fock radial wave functions* are used in the present calculation for the entire  $3snd\ ^1D$  series.

To simplify our calculation, the *Hartree-Fock radial wave functions* are used for *all* doubly excited configurations. In addition, we have also carried out a *separate* calculation with all configurations represented by simple *Hartree-Fock radial wave functions* for the  $^1S$  and  $^1P$  series to examine the convergence pattern. The energy contributions due to the dipole polarization and the dielectronic potential are also included.

### III. RESULTS AND DISCUSSION

For the  $3sns\ ^1S$  series, the effect of the configuration interaction is illustrated in Fig. 1. Comparison between the calculated spectra  $B$  and  $C$  to the spectrum  $A$  clearly shows that the configuration mixing from  $4s^2$  and  $3d^2$  to the  $3s^2$  ground state is very small. On the other hand, from spectrum  $D$  it is evident that the strong mixing between the  $3p^2$  doubly excited perturber and the  $3s^2$  configuration dominates the energy correction to the ground state. The interaction between the  $3p(4-6)p$  and  $3sns$  series is small but non-negligible as shown in spectra  $E$  and  $F$ . The nearly identical result between spectrum  $F$  and the converged result  $G$  indicates that the higher excited configurations contribute very little to the energy correction of the term values of the  $3sns$  series.

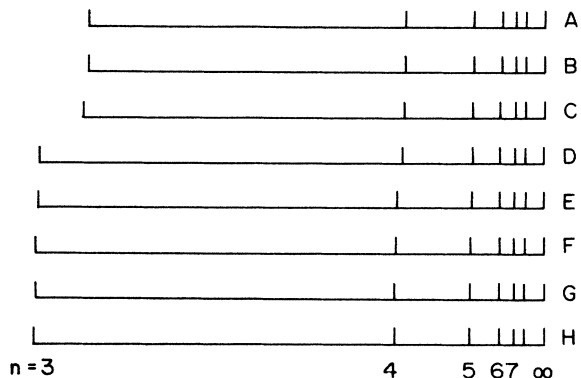


FIG. 1. Energy spectra for the  $Mg\ 3sns\ ^1S$  series. The energy is relative to the first ionization threshold at the extreme right. Spectrum  $H$  represents the experimental data from Ref. 12. Spectrum  $G$  is the converged result from the present calculation. Configurations included in the calculation of spectra  $A-F$  are  $A$ ,  $3s(3-10)s$ ;  $B$ ,  $3s(3-10)s + 4s^2$ ;  $C$ ,  $3s(3-10)s + 3d^2$ ;  $D$ ,  $3s(3-10)s + 3p^2$ ;  $E$ ,  $3s(3-10)s + 3p(3-4)p + 3d^2 + 4s^2$ ;  $F$ ,  $3s(3-10)s + 3p(3-6)p + 3d(3-5)d + 4s(4-5)s$ .

Table I compares the result of the present calculation, in terms of the quantum defect, with the available experimental<sup>12</sup> and theoretical<sup>2-5,7</sup> results. For higher excited states the agreement between the present calculation and the experimental data is excellent. For the  $3s^2$  ground state the Hartree-Fock result is shown to be in better agreement with the observed value. The probability density contribution to the  $3s^2$  ground state from the  $p^2$  configurations is about 6.3% in our calculation which is consistent with the multiconfiguration Hartree-Fock calculation of Fischer.<sup>2</sup>

Figure 2 illustrates the energy correction to the  $3snp\ ^1P$  series due to the configuration interaction. From spectra  $B$  and  $C$  one could conclude that the influence from the  $3pns$  and  $4snp$  to the  $3snp$  series is small. On the other hand, it is clear from spectrum  $D$  that the energy correc-

TABLE I. Quantum defect for the  $Mg\ 3sns\ ^1S$  states.

State	Expt. (Ref. 12)	Theory						
		a	b	c	d	e	f	g
$3s\ 3s$	1.6661	1.6441	1.6604	1.6595	1.656	1.655	1.653	1.649
$3s\ 4s$	1.5423	1.5360	1.5272	1.5342	1.533	1.532	1.514	1.52
$3s\ 5s$	1.5302	1.5254	1.5139	1.5188	1.520		1.499	1.50
$3s\ 6s$	1.5268	1.5257			1.516		1.492	1.49
$3s\ 7s$	1.5255	1.5295			1.515		1.478	1.50
$3s\ 8s$	1.5251	1.5212						
$3s\ 9s$	1.5249	1.5163						

<sup>a</sup>Present calculation with Hartree-Fock  $3s^2$  configuration and interaction potential for excited  $3sns$  configurations.

<sup>b</sup>Present calculation with simple Hartree-Fock radial wave functions.

<sup>c</sup>Mendoza, Ref. 7.

<sup>d</sup>Fischer, Ref. 2.

<sup>e</sup>Weiss, Ref. 3.

<sup>f</sup>Laughlin and Victor, Ref. 4.

<sup>g</sup>Bates and Altick, Ref. 5.

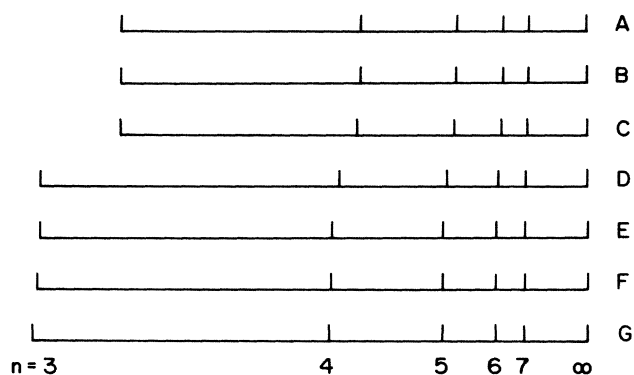


FIG. 2. Energy spectra for the Mg  $3snp\ ^1P$  series. The energy is relative to the first ionization threshold at the extreme right. Spectrum *G* represents the experimental data from Ref. 12. Spectrum *F* is the converged result from the present calculation. Configurations included in the calculation of spectra *A–E* are *A*,  $3s(3-10)p$ ; *B*,  $3s(3-10)p+4s(4-10)p$ ; *C*,  $3s(3-10)p+3p(4-11)s$ ; *D*,  $3s(3-10)p+3p(3-10)d$ ; *E*,  $3s(3-10)p+3p(4-11)s+3p(3-10)d$ .

tion to the term values of the  $3snp\ ^1P$  series is dominated by the configuration interaction due to the  $3pnd$  configuration series. The spectrum *E* shows that the combined interaction from the  $3pns$  and  $3pnd$  series is sufficient in leading to a numerical result closed to the final converged spectrum *F*. Table II compares the quantum defect from the present calculation to the available experimental<sup>12</sup> and theoretical<sup>2-5,7,8</sup> results. For the higher excited states the present calculation with the interaction potential is in very good agreement with the experimental data. For the lower excited states the best agreement with the experimental result is obtained in the straightforward Hartree-Fock calculation.

Figure 3 illustrates the effect of the configuration in-

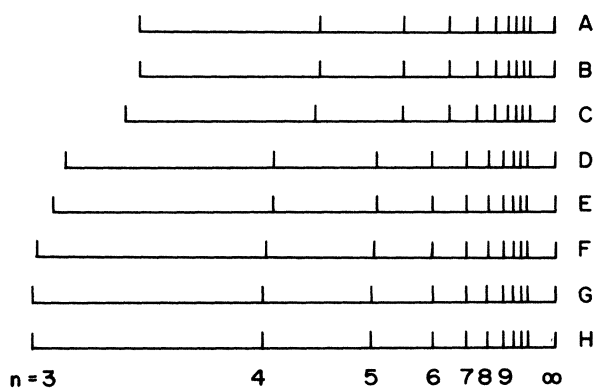


FIG. 3. Energy spectra for the Mg  $3snd\ ^1D$  series. The energy is relative to the first ionization threshold at the extreme right. Spectrum *H* represents the experimental data from Ref. 12. Spectrum *G* is the converged result from the present calculation. Configurations included in the calculation of spectra *A–F* are *A*,  $3s(3-16)d$ ; *B*,  $3s(3-16)d+3d^2$ ; *C*,  $3s(3-16)d+3p4f$ ; *D*,  $3s(3-16)d+3p^2$ ; *E*,  $3s(3-16)d+3p^2+3p4f+3d^2$ ; *F*,  $3s(3-16)d+3p(3-6)p+3p(4-5)f$ .

teraction to the energy correction of the  $3snd\ ^1D$  series. The nearly identical energy values between spectra *A* and *B* shows that the influence of the  $3d^2$  configuration to the  $3snd$  series is negligible. The difference between *C* and *A* suggests that the influence of the  $3p4f$  configuration is small but noticeable for the lower excited states. The main energy correction to the  $3snd$  series clearly comes from the  $3pn(\geq 3)p$  configuration series as shown by the spectra *D* and *F*. In particular, spectrum *D* shows that the entire  $3snd$  series is shifted due to the strong interaction with the  $3p^2$  configuration. This is consistent with the conclusion of Lu from the simple quantum defect analysis.<sup>9</sup> The spectrum *G* includes configuration interaction from the  $3pnp$  (and  $nf$ ),  $3dnd$ ,  $4snd$ , and  $4pnp$  (and

TABLE II. Quantum defect for the Mg  $3snp\ ^1P$  states.

State	Expt. (Ref. 12)	Theory								
		a	b	c	d	f	e	f	g	h
$3s\ 3p$	0.9696	0.9578		0.9533	0.9544		0.9519	0.935	0.942	1.019
$3s\ 4p$	1.0160	1.0028		1.0069	1.0028			0.978	0.985	1.087
$3s\ 5p$	1.0305	1.0209	1.0127	1.0214	1.0316			0.997	0.997	
$3s\ 6p$	1.0375	1.0356	1.0356		1.0273			1.000	1.000	
$3s\ 7p$	1.0414	1.0475	1.0509		1.0281					
$3s\ 8p$	1.0438		1.0604							
$3s\ 9p$	1.0457		1.0450							

<sup>a</sup>Present calculation with simple Hartree-Fock radial wave functions.

<sup>b</sup>Present calculation with simple Hartree-Fock  $3s\ 3p$  configuration and interaction potential for excited  $3snp$  configurations.

<sup>c</sup>Mendoza, Ref. 7.

<sup>d</sup>Fischer, Ref. 2.

<sup>e</sup>Weiss, Ref. 3.

<sup>f</sup>Laughlin and Victor, Ref. 4.

<sup>g</sup>Bates and Altick, Ref. 5.

<sup>h</sup>O'Mahony and Greene, Ref. 8.

TABLE III. Quantum defect for the Mg  $3snd\ ^1D$  states.

State	Expt. (Ref. 12)	Present	Theory		
			Mendoza (Ref. 7)	Fischer (Ref. 2)	Weiss (Ref. 3)
$3s\ 3d$	0.3191	0.3158	0.3111	0.3487	0.264
$3s\ 4d$	0.4146	0.4150	0.4042	0.4453	
$3s\ 5d$	0.4764	0.4811	0.4639	0.5053	
$3s\ 6d$	0.5152	0.5240		0.5397	
$3s\ 7d$	0.5405	0.5472		0.5638	
$3s\ 8d$	0.5573	0.5582		0.575	
$3s\ 9d$	0.5689	0.5662			
$3s\ 10d$	0.5772	0.5728			
$3s\ 11d$	0.5833	0.5777			

$nf$ ) series. This is approximately equivalent to the five-state close-coupling scattering calculation.<sup>6,7</sup> Consequently, it is not unexpected to find that the theoretical values of the quantum defect in the present calculation are in slightly better agreement with the experimental data than the three-state close-coupling calculation of Mendoza<sup>7</sup> as shown in Table III. The probability density contributions to the  $3snd\ ^1D$  series from the  $p^2$  configurations are approximately 19%, 12%, 7%, 4%, 3%, 2%, and 1% for the  $3s(3-9)d$  states, respectively. It is, again, consistent with the estimation of Fischer.<sup>2</sup>

In summary, the present calculation has demonstrated successfully that a *simple* superposition of configuration wave function approach can be effective in the quantitative determination of the term values of the singly excited states for the Mg atom. For singlet series with small  $n$  dependence in quantum defect each individual highly excited state is dominated by a single configuration with its wave function generated in a nonlocal interaction potential. For states with large  $n$  variation in quantum defect,

it is found that the straightforward superposition of configuration approach with the simple Hartree-Fock wave function actually leads to the best numerical result. Numerically, the use of the Hartree-Fock wave function generally requires a larger numbers of configurations in the calculation for the converged result. For instance, in the  $3snd$  series calculation, a total of 14  $3snd$  configurations are included to get the converged results for the eight lower states. Despite this additional numerical effort, we should point out that all numerical work in the present calculation was carried out on a table-top personal computer.

#### ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant No. PHY84-08333. We would also like to acknowledge the support of the IBM Socrates Program at USC.

<sup>1</sup>T. F. Gallagher, *Electronic and Atomic Collisions*, edited by D. C. Lorents, W. E. Meyerhof, and J. R. Peterson (North-Holland, Amsterdam, 1986), p. 609.

<sup>2</sup>C. F. Fischer, *Can. J. Phys.* **53**, 184 (1975); **53**, 338 (1975).

<sup>3</sup>A. W. Weiss, *J. Chem. Phys.* **47**, 3573 (1967).

<sup>4</sup>C. Laughlin and G. A. Victor, *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), Vol. 3, p. 247.

<sup>5</sup>G. Bates and P. L. Altick, *J. Phys. B* **6**, 653 (1973).

<sup>6</sup>D. W. Norcross and M. J. Seaton, *J. Phys. B* **9**, 2983 (1976).

<sup>7</sup>C. Mendoza, *J. Phys. B* **14**, 397 (1981).

<sup>8</sup>P. F. O'Mahony and C. H. Greene, *Phys. Rev. A* **31**, 250 (1985).

<sup>9</sup>K. T. Lu, *J. Opt. Soc. Am.* **64**, 706 (1974).

<sup>10</sup>T. N. Chang and Y. S. Kim, *Phys. Rev. A* **34**, 2609 (1986).

<sup>11</sup>C. Bottcher and A. Dalgarno, *Proc. R. Soc. London, Ser. A* **340**, 187 (1974).

<sup>12</sup>W. C. Martin and R. Zalubas, *J. Phys. Chem. Ref. Data* **9**, 1 (1980).