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Theoretical study of the two-electron interaction in alkaline-earth atoms

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We present a theoretical treatment for the two-electron interaction in the alkaline-earth atoms. The most important element in this procedure is the introduction of a nonlocal interaction potential for states of fixed total spin S and total orbital angular momentum L. The orbital wave function generated in this potential is capable of prediagonalizing the N-particle Hamiltonian matrix with respect to a given two-electron configuration series (i.e., a series of configurations with one valence electron in fixed orbital nl and the other one with fixed orbital angular momentum l' but variable principal quantum number n'). With this procedure, we will show that the wave function for each state is well represented by a simple superposition of a few neighboring configurations. The effectiveness of this approach to include higher excited states in a simple calculation is demonstrated in its application to the ^1P states of the Mg atom.

I. INTRODUCTION

One of the most interesting features in the spectra of the alkaline-earth atoms is the autoionization structure dominated by the doubly excited states at energy above the first ionization threshold. The use of various configuration-interaction methods[1-4] and the more elaborate scattering technique,[5] with the dominating doubly excited configurations explicitly included, is capable of leading to agreement between the theoretical estimation and the experimental measurement in the quantitative determination of the energy positions and in the qualitative interpretation of the overall shape of the *first few* autoionization states above the ionization threshold. Despite their success, without further modification, a *straightforward* extension of these existing methods to include higher states in the autoionization series would require enormous numerical efforts and consequently reduce its effectiveness.

It is the purpose of this paper to introduce a set of orbital wave functions generated in a nonlocal interaction potential which minimizes analytically the mixing between the two-particle orbital wave functions representing different excited configurations. This nonlocal potential is determined by its ability to prediagonalize the nonrelativistic N-particle Hamiltonian matrix with respect to a given configuration series $(nl,n'l')$ with one orbit nl fixed and the value of l' of the other orbit $n'l'$ fixed. In other words, the interaction between members (including the continuum) of a configuration series is represented by this potential without approximation. Therefore, the numerical accuracy of the calculated energy eigenvalues for the higher Rydberg states in this configuration series remains the same. With the two-electron interaction included in this interaction potential, we are able to show that the configuration mixing is usually limited to few neighboring states (normally two to three configurations) from other configuration series of the same L and S symmetry. Consequently, only a small number of configurations are needed to reach the desirable numerical convergence. Moreover, as the wave function for each state is dominated by a single configuration with minor contribution from two to three neighboring states, the state can be identified by this configuration with little ambiguity.

II. THEORY

In the present theoretical procedure, the N-particle nonrelativistic Hamiltonian is given by

$$\hat{H}=\sum_{i=1}^{N} h_0(\mathbf{r}_i)+\sum_{\substack{i,j\\(i<j)}}^{N}\frac{1}{r_{ij}} \tag{1}$$

and

$$h_0(\mathbf{r})=-\frac{1}{2}\frac{d^2}{dr^2}-\frac{Z}{r}+\frac{1}{2}\frac{\mathbf{L}^2}{r^2}\,, \tag{2}$$

where Z is the nuclear charge and $\mathbf{L}$ is the orbital angular momentum operator. The energy eigenvalues of the atomic states in the LS coupling with given S and L can be evaluated by diagonalizing the Hamiltonian matrix constructed with the N-particle configuration wave function $\Psi^{SL}_{n_il_i,n_jl_j}$ corresponding to the electronic configuration (n_il_i,n_jl_j) for the two valence electrons. This configuration wave function Ψ is given by the sum of N-particle Slater determinant wave functions over the magnetic quantum numbers m and m_s with each Slater determinant consisting of N one-particle electronic orbital wave functions, i.e.,

$$\Psi^{SL}_{n_il_i,n_jl_j}=\sum_{\text{all } m\text{'s}}(-1)^{l_j-l_i}[(2S+1)(2L+1)]^{1/2}\begin{pmatrix} l_i & l_j & L\\ m_i & m_j & M\end{pmatrix}\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S\\ m_{s_i} & m_{s_j} & M_s\end{pmatrix}\phi^{m_im_{s_i}m_jm_{s_j}}_{n_il_i,n_jl_j} \tag{3}$$

and

$$\phi_{n_il_i,n_jl_j}^{m_im_{s_i}m_jm_{s_j}}(\mathbf{r}_i,\ldots,\mathbf{r}_N)=(N!)^{-1/2}\det\nolimits_N|u_\alpha(\mathbf{r}_\mu)| , \tag{4}$$

where the orbital wave function u_α is given by the product of its spatial and the spin part, i.e.,

$$u_\alpha(\mathbf{r}_\mu)=\chi_{n_\alpha l_\alpha}(r_\mu)Y_{l_\alpha m_\alpha}(\Omega_\mu)\sigma_{m_{s_\alpha}} . \tag{5}$$

The first $N-2$ of the u_α in ϕ represent the orbital wave functions for the $N-2$ core orbits ranging from $1s^2$ to np^6 (e.g., $n=2$ for Mg, $n=3$ for Ca, etc.). The last two orbital wave functions are given by $\alpha_{N-1}=(n_il_im_im_{s_i})$ and $\alpha_N=(n_jl_jm_jm_{s_j})$ which correspond to the orbit of the two valence electrons. If $n_il_i=n_jl_j$, a factor of $2^{-1/2}$ should be included in Eq. (3) to ensure the normalization. With Ψ given by Eq. (3), a straightforward derivation will lead to a general expression for the matrix element in the Hamiltonian matrix,

$$\begin{aligned}\langle\Psi^{SL}_{n_i'l_i',n_j'l_j'}|\hat{H}|\Psi^{SL}_{n_il_i,n_jl_j}\rangle={}&[\delta_{n_i'n_i}\delta_{l_i'l_i}\delta_{n_j'n_j}\delta_{l_j'l_j}+(-1)^{l_i+l_j+L+S}\delta_{n_i'n_j}\delta_{l_i'l_j}\delta_{n_j'n_i}\delta_{l_j'l_i}]E^{\mathrm{HF}}_{\mathrm{core}}\\&+\delta_{l_i'l_i}\delta_{l_j'l_j}(\delta_{n_i'n_i}\langle n_j'l_j'|h^{\mathrm{HF}}_{l_j}|n_jl_j\rangle+\delta_{n_j'n_j}\langle n_i'l_i'|h^{\mathrm{HF}}_{l_i}|n_il_i\rangle)\\&+(-1)^{l_j+l_i+L+S}\delta_{l_i'l_j}\delta_{l_j'l_i}(\delta_{n_i'n_j}\langle n_j'l_j'|h^{\mathrm{HF}}_{l_i}|n_il_i\rangle+\delta_{n_j'n_i}\langle n_i'l_i'|h^{\mathrm{HF}}_{l_j}|n_jl_j\rangle)\\&+(-1)^{l_j'-l_i}\left[\sum_k(-1)^L\begin{Bmatrix}l_i'&l_j'&L\\l_j&l_i&k\end{Bmatrix}\langle n_i'l_i'n_j'l_j'||V^k||n_il_in_jl_j\rangle\right.\\&\left.\qquad+\sum_k(-1)^S\begin{Bmatrix}l_i'&l_j'&L\\l_i&l_j&k\end{Bmatrix}\langle n_i'l_i'n_j'l_j'||V^k||n_jl_jn_il_i\rangle\right] ,\end{aligned}\tag{6}$$

where $E^{\mathrm{HF}}_{\mathrm{core}}$ is the total Hartree-Fock energy for the $N-2$ core electrons calculated with the orbital wave function generated by the one-electron radial Hartree-Fock Hamiltonian

$$\begin{aligned}h_l^{\mathrm{HF}}(r)f_l(r)={}&\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{Z}{r}+\frac{1}{2}\frac{l(l+1)}{r^2}\right]f_l(r)+\sum_{n'l'}^{\mathrm{core}}2\left[\frac{2l'+1}{2l+1}\right]^{1/2}(l||V^0(\chi_{n'l'},\chi_{n'l'};r)||l)f_l(r)\\&-\frac{1}{2l+1}\sum_{n'l'}^{\mathrm{core}}\sum_\nu(-1)^\nu(l||V^\nu(\chi_{n'l'},f_l;r)||l')\chi_{n'l'}(r) ,\end{aligned}\tag{7}$$

for the $N-2$ core orbitals and the matrix element $\langle ab||V^k||cd\rangle$ is the two-particle Coulomb matrix. (We refer to Ref. 6 for a detailed description for the notation employed in this paper.)

To derive the nonlocal potential, we apply the condition that the Hamiltonian matrix with respect to a single configuration series (e.g., $n_i'l_i'=n_il_i$ and $l_j'=l_j$) is diagonal, i.e.,

$$\langle\Psi^{SL}_{n_il_i,n_j'l_j}|\hat{H}|\Psi^{SL}_{n_il_i,n_jl_j}\rangle=\delta_{n_j'n_j}(E^{\mathrm{HF}}_{\mathrm{core}}+\epsilon_{n_il_i}+\epsilon_{n_jl_j}) . \tag{8}$$

This condition is satisfied if the one-particle radial wave functions χ for the fixed orbit n_il_i and the variable orbit n_jl_j are defined by

$$h^{\mathrm{HF}}_{l_i}(r)\chi_{n_il_i}(r)=\epsilon_{n_il_i}\chi_{n_il_i}(r) \tag{9}$$

and

$$[h^{\mathrm{HF}}_{l_j}(r)+(1-P_{l_j})V^{l_j}(r)]\chi_{n_jl_j}(r)=\epsilon_{n_jl_j}\chi_{n_jl_j}(r) , \tag{10}$$

respectively, with the nonlocal interaction potential $V^{l_j}(r)$ given by

$$\begin{aligned}V^{l_j}(r)f_{l_j}(r)={}&(-1)^{l_j-l_i}\sum_\nu\left[(-1)^L\begin{Bmatrix}l_i&l_j&L\\l_j&l_i&\nu\end{Bmatrix}(l_j||V^\nu(\chi_{n_il_i},\chi_{n_il_i}r)||l_j)f_{l_j}(r)\right.\\&\left.\qquad+(-1)^S\begin{Bmatrix}l_i&l_j&L\\l_i&l_j&\nu\end{Bmatrix}(l_j||V^\nu(\chi_{n_il_i},f_{l_j};r)||l_i)\chi_{n_il_i}(r)\right] .\end{aligned}\tag{11}$$

The radial wave functions $\chi_{n_jl_j}$ defined by Eq. (10) are orthogonal to all the Hartree-Fock core radial wave functions with the help of the projection operator P_{l_j} which projects out all core orbitals.

With the sub-Hamiltonian matrix prediagonalized with respect to a given configuration series, the total Hamiltonian matrix is greatly simplified and the only nonzero off-diagonal matrix elements are those between configurations from different configuration series. To calculate the energy eigenvalue of each state, we simply diagonalize the total Hamiltonian matrix. And at the same time, we obtain the corresponding N-particle multiconfiguration state wave function

$$\Phi = \sum_{n_il_i,n_jl_j} C^{SL}(n_il_i,n_jl_j)\Psi^{SL}_{n_il_i,n_jl_j}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,, \qquad (12)$$

where $|C^{SL}(n_il_i,n_jl_j)|^2$ is the probability density for the configuration (n_il_i,n_jl_j) for the given state.

III. RESULTS AND DISCUSSION

To demonstrate the effectiveness of this theoretical procedure, we present the result of its application to the $(3pns)\,{}^1P$ and $(3pnd)\,{}^1P$ doubly excited configuration series of the Mg atom. The first step of our numerical calculation is to solve Eq. (9) for the $3p$ orbit and Eq. (10) for the ns and nd orbits. By setting the energy level of the ground state of the Mg III ion equal to zero, following Eq. (8), the energy of the $3pnl$ state is simply the sum of the orbital energy eigenvalues ϵ_{3p} and ϵ_{nl}. Table I compares the energy of the $3pnl$ state from this *single-configuration* calculation (column C) with the experimental data compiled by Martin and Zalubas.[7] Although it appears that the result of this "zeroth-order" calculation is noticeably different from that of the experimental data, a closer examination indicates that the energy *separation* between adjacent states in these two overlapping configuration series is actually in good agreement with the observed value. And this discrepancy in energy can be attributed to the difference between the calculated $3p$ threshold (i.e., ϵ_{3p}) and that of the actual experimental $3p$ threshold. Since this difference is primarily due to the core polarization effect, a more appropriate comparison of the theoretical estimation with the experimental data should include the contribution from this effect.

To estimate the contribution from the core dipole polarization, we evaluate its energy correction with a simple model potential similar to that used by other earlier calculations,[2,5] i.e.,

$$V_p(r) = -\frac{\alpha}{r^4}\left(1-e^{-(r/r_0)^6}\right) \qquad (13)$$

where $\alpha = 0.489$ a.u. is the core dipole polarizability[8] and the cutoff radius $r_0 = 1.096a_0$ is fitted so that the energy correction is equal to the difference (i.e., $\Delta = 0.011\,92$ Ry) between the calculated ϵ_{3p} and the experimental threshold. By using this parametrized potential, the energy contribution due to the core polarization effect is given by

$$\Delta E_p(nl) = \langle \Psi^{SL}_{3pnl} \mid V_p \mid \Psi^{SL}_{3pnl} \rangle \,. \qquad (14)$$

Column B in Table I shows that the resulting *single-configuration* calculation including the core polarization effect agrees very well with the experimental data for all higher Rydberg states in the $3pns$ and $3pnd$ configuration series.

The interaction between the $3pns$ and $3pnd$ configuration series is taken into account in the second step of our calculation by diagonalizing the Hamiltonian matrix with both series included. The energy corrections due to the core dipole polarization and the dielectronic potential introduced by Bottcher and Dalgarno[2,5,9] are also included in the Hamiltonian matrix with the same set of parame-

TABLE I. Comparison of the experimental energy levels with the results of various theoretical calculations. All energy values are given in Rydberg units. Energy is set to zero at the ground state of Mg III. The experimental data are taken from Ref. 7. In column A, only $3pn(4-11)s$ and $3pn(3-10)d$ are included in the diagonalization; in column B, the single configuration result is given; and in column C, the single configuration result without the core polarization is given.

State	Expt.	Theory				
		Present	A	B	C	HF
$3p\,4s$	−0.9503	−0.9590	−0.9508	−0.9462	−0.9330	−0.9640
$3p\,3d$	−0.8841	−0.8865	−0.8783	−0.8789	−0.8669	−0.8908
$3p\,5s$	−0.8646	−0.8656	−0.8625	−0.8628	−0.8504	−0.8673
$3p\,4d$	−0.8399	−0.8401	−0.8368	−0.8371	−0.8251	−0.8424
$3p\,6s$	−0.8302	−0.8306	−0.8290	−0.8295	−0.8174	−0.8314
$3p\,5d$	−0.8183	−0.8185	−0.8168	−0.8170	−0.8050	−0.8198
$3p\,7s$	−0.8134	−0.8134	−0.8124	−0.8129	−0.8008	−0.8139
$3p\,6d$	−0.8067	−0.8067	−0.8056	−0.8058	−0.7939	−0.8075
$3p\,8s$	−0.8035	−0.8036	−0.8030	−0.8033	−0.7913	−0.8039
$3p\,7d$	−0.7994	−0.7995	−0.7988	−0.7990	−0.7871	−0.7999
$3p\,9s$	−0.7974	−0.7975	−0.7971	−0.7974	−0.7854	−0.7967
$3p\,8d$	−0.7947	−0.7948	−0.7944	−0.7945	−0.7826	−0.7910
$3p\,10s$	−0.7933	−0.7935	−0.7932	−0.7934	−0.7814	−0.7810
$3p\,9d$	−0.7915	−0.7916	−0.7913	−0.7914	−0.7795	−0.7594

TABLE II. Breakdown of the probability density in percentage (%) for the doubly excited $3pns\,(^1P)$ and $3pnd\,(^1P)$ states of Mg obtained in the present calculation. The main contribution (over 96%) to the probability density for each state is dominated by two to three neighboring configurations.

Configuration	State							
	$3p\,4s$	$3p\,5s$	$3p\,6s$	$3p\,7s$	$3p\,3d$	$3p\,4d$	$3p\,5d$	$3p\,6d$
$3p\,4s$	93.7				3.9			
$3p\,3d$	3.1	5.9			88.0	1.0		
$3p\,5s$		90.7			4.4	3.1		
$3p\,4d$		1.6	5.7			89.0	1.0	
$3p\,6s$			91.7			4.2	2.4	
$3p\,5d$			1.2	5.1			90.3	
$3p\,7s$				92.7			3.8	2.0
$3p\,6d$				1.0				91.5
$3p\,8s$								3.4
$3d\,4p$	1.6							
$3d\,4f$					1.2			

ters α and r_0 given earlier. As shown by the column A in Table I, the configuration mixing between these two overlapping configuration series only introduces a small energy correction. This is mainly due to the cancellation between the energy corrections from two neighboring configurations on the opposite sides of each state except for the $3p\,4s$ state where only one neighboring configuration $3p\,3d$ is present. This accounts for the relatively large correction seen for the $3p\,4s$ state.

The effect due to other higher doubly excited states can also be examined by including their corresponding configurations in the diagonalization of the Hamiltonian matrix. The converged energy eigenvalue to four effective figures for the $3pns$ and $3pnd$ series are reached when approximately 20 additional configurations are included. The final result, including the core polarization contribution (column "Present" in Table I), is in excellent agreement with the experimental data. We should point out that one of the most important advantages of the present procedure is its ability to obtain very accurate energy values for the *higher Rydberg states* which is often found difficult in other methods.

The interaction between the doubly excited states and the singly excited $3snp$ and its corresponding $3s\epsilon p$ continuum, which are responsible for the width and a small energy shift of the doubly excited state, is not included in the result of the present calculation. This is due to the difficulty in achieving converged energy value when only finite number of the bound configurations $3snp$ can be included in the Hamiltonian matrix. For lower states, this interaction accounts for the small discrepancy between theory and experiment shown in Table I. A more satisfactory theoretical treatment of the autoionization widths and shifts can be included by combining the present procedure with the method developed by Fano[10] and Bates and Altick.[1] A complete study of the autoionization state will be presented in a separate paper.

We have also carried out a similar calculation with *all* radial orbital wave functions generated by the one-particle Hartree-Fock Hamiltonian, i.e., Eqs. (7) and (9). To achieve the desired convergence, approximately 60 configurations are included. Table I shows that the Hartree-Fock result is generally satisfactory except for the higher states (e.g., the relatively poor energy values for the $3p\,10s$ and $4p\,9d$ states) where an accurate energy calculation would require many additional configurations. The results of the present calculation for lower excited states are also in good agreement with other earlier calculations.[1,2,5]

Finally, in Table II, we list the probability density (i.e., $|\,C^{SL}\,|^2$) calculated from the state wave function Φ for some of the states in the $3pns$ and $3pnd$ series. The main contribution (over 96%) to the probability density for each state is dominated by two to three neighboring configurations which is consistent with the experimentally observed spectrum.[11] As we indicated earlier, the state wave function Φ is dominated by a single configuration and the state can be readily characterized by its corresponding wave function with little ambiguity.

In addition to the application to the doubly excited states, we have found that with a minor modification, the present procedure is also effective when applied to the energy estimation of the ground and the singly excited bound states. With the state wave function well characterized by a simple superposition of few neighboring configuration wave functions, we can readily extend our study to other dynamical processes for the alkaline-earth atoms. The result of these studies will be reported elsewhere.

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[1] G. Bates and P. L. Altick, J. Phys. B **6**, 653 (1973).
[2] C. Laughlin and G. A. Victor, *Atomic Physics 3*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), p. 247.
[3] J. Dubau and J. Wells, J. Phys. B **6**, 1452 (1973).
[4] P. F. O'Mahony and C. H. Greene, Phys. Rev. A **31**, 250 (1985).
[5] C. Mendoza, J. Phys. B **14**, 397 (1981).
[6] T. N. Chang and U. Fano, Phys. Rev. A **13**, 263 (1976).
[7] W. C. Martin and R. Zalubas, J. Phys. Chem. Ref. Data **9**, 1 (1980).
[8] U. Opik, Proc. Phys. Soc. **92**, 566 (1967).
[9] C. Bottcher and A. Dalgarno, Proc. R. Soc. A **340**, 187 (1974).
[10] U. Fano, Phys. Rev. **124**, 1866 (1961).
[11] G. Mehlman-Balloffet and J. M. Esteva, Astrophys. J. **157**, 945 (1969).