Relativistic random-phase approximation calculations on the zinc isoelectronic sequence

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Excitation energies, oscillator strengths, and transition probabilities for the $4s^2\ {}^1S_0$-$4s4p\ {}^1P_1$, $4s^2\ {}^1S_0$-$4s5p\ {}^1P_1$, and $4s^2\ {}^1S_0$-$4s6p\ {}^1P_1$ resonance transitions of elements of the zinc isoelectronic sequence are calculated using the relativistic random-phase approximation. The elements considered range from Ga II to U LXIII and include many of interest in current fusion research. A graphical analysis of the systematic trends of the oscillator strength as a function of the inverse nuclear charge provides a means of estimating the oscillator strengths for those elements whose values are not explicitly calculated.

I. INTRODUCTION

Accurate values for the oscillator strengths of highly ionized elements of the zinc isoelectronic sequence are needed in the study of high-temperature plasmas.[1] Approximately 40% of the radiative losses from tokamak plasmas are due to heavy-metal impurities,[2] and many of the metals suggested as first wall materials will be ionized to a zinclike configuration.

In order to calculate reliable oscillator strengths, the effect of interelectron correlation must be taken into account. As the stage of ionization increases, relativistic effects become sizable and must be included in the theory.[3] The relativistic random-phase approximation[4] (RRPA) incorporates the most important correlation effects and by treating the relativistic effects nonperturbatively allows the calculations to be performed throughout the isoelectronic sequence. The method has been used previously to calculate transition rates and oscillator strengths for elements of the He isoelectronic sequence by Johnson, Lin, and Dalgarno,[4(a-c)] for elements of the Be isoelectronic sequence by Lin and Johnson,[4(d)] and for elements of the Mg isoelectronic sequence by Shorer, Lin, and Johnson.[4(e)]

Using the RRPA, we calculate the excitation energies, oscillator strengths, and transition probabilities for the $4s^2\ {}^1S_0$-$4s4p\ {}^1P_1$, $4s5p\ {}^1P_1$, and $4s6p\ {}^1P_1$ resonance transitions of elements of the zinc isoelectronic sequence. Earlier studies[4(d)] have shown that correlation with the inner-shell electrons is of minor importance when the dipole length formulation is used, and we include only the intrashell correlation arising from the interaction between the valence electrons.

II. THEORY

Details of the derivation of the equations of the RRPA and a method for their numerical solution have been given in previous papers.[4] Only a summary of the essential features will be given here.

The equations of the RRPA are derived by a procedure based on the time-dependent Hartree-Fock (TDHF) method.[5] An external field $A_+\exp(-i\omega t)+A_-\exp(+i\omega t)$ induces perturbations $w_{i\pm}$ in the Dirac-Hartree-Fock (DHF) occupied-state orbitals u_i. These perturbations are given by the RRPA equations

$$(h_0+V-\epsilon_i\mp\omega)w_{i\pm}=(A_\pm-V_\pm^{(1)})u_i,\quad i=1,2,\ldots,N,$$

where h_0 is the one-electron Dirac operator, V is the DHF potential, ϵ_i is the DHF orbital eigenvalue, and $V_\pm^{(1)}$, given explicitly in natural units by

$$V_\pm^{(1)}u_i=\sum_{j=1}^{N}e^2\int\frac{d\vec{r}'}{|\vec{r}-\vec{r}'|}[(u_j^*w_{j\pm})'u_i+(w_{j\mp}^*u_j)'u_i$$
$$-(w_{j\mp}^*u_i)'u_j-(u_j^*u_i)'w_{j\pm}],$$

represents the correlation effects included in the RRPA.

By writing the orbitals and perturbations in a spherical basis, the RRPA equations are reduced to coupled equations for the radial factors, which are solved by a combination of Green's function[6] and iterative methods. The zero-order solution represents a DHF intermediate coupling result. The nonrelativistic LS designations are used to label the intermediate-coupling solutions.

Appropriate choices of gauge[7] for the transition operator yield oscillator strengths which reduce to the length and velocity forms in the nonrelativistic limit. As in the nonrelativistic case,[8] the two results are equivalent in the RRPA[4(b)] when the full set of equations is solved exactly. The neglect of the inner-shell correlation effects causes a difference between the two values and the mag-

TABLE I. $4s^2\ {}^1S_0$-$4s4p\ {}^1P_1$ RRPA excitation energies (in a.u.) and oscillator strengths (length form) compared with DHF intermediate coupling results and other values.

		Excitation energy				Oscillator strength			
Z	Ion	E(RRPA)	E(DHF)	E(other)	E(expt.)	f(RRPA)	f(DHF)	f(other)	f(expt.)
31	Ga^{+1}	0.3077	0.2984	0.3017[a]	0.3221[b]	1.97	2.30	2.26[c]	1.39[d]
32	Ge^{+2}	0.4093	0.3954	0.4023	0.4186	1.98	2.30	2.25	1.38
35	Br^{+5}	0.6886	0.6693	0.681[e]	0.6893	1.84	2.13	1.91[e]	0.82[f]
40	Zr^{+10}	1.1501	1.1314		1.1438[g]	1.61	1.86		
42	Mo^{+12}	1.3445	1.3268	1.32	1.3365	1.54	1.77	1.57	
54	Xe^{+24}	2.7853	2.7725	2.74	2.77[h]	1.24	1.39	1.24	
62	Sm^{+32}	4.1966	4.1846			1.15	1.26		
74	W^{+44}	7.5292	7.5154	7.57		1.15	1.23	1.16	
79	Au^{+49}	9.5570	9.5417	9.67		1.19	1.26	1.20	
92	U^{+62}	17.6294	17.6087			1.37	1.41		

[a] Zilitis, Ref. 9.
[b] Moore-NBS, Ref. 10.
[c] Warner, Ref. 11.
[d] Sørensen, Ref. 12.
[e] Cowan, Ref. 13.
[f] Pinnington, Kernahan, and Donnelly, Ref. 14.
[g] Reader and Acquista, Ref. 15.
[h] Hinnov, Rev. 16.

nitude of the difference provides an indication of the importance of the inner-shell effects. Because the length form places less emphasis on the part of the wave function near the nucleus, it should be the more reliable.

III. RESULTS AND DISCUSSION

Table I presents the RRPA excitation energies in atomic units and compares them with DHF intermediate coupling and other values. Table II lists the RRPA resonance transition wavelengths and includes experimental measurements for Zr XI and Mo XIII by Reader and Acquista[15] and for Xe XXV by Hinnov.[16] The RRPA values appear in general to be slightly more accurate than the DHF results and lie within 1% of the experimental data for the more highly ionized elements. Figure 1 shows the RRPA excitation energies divided by the nuclear charge Z, as a function of Z^{-1}. The

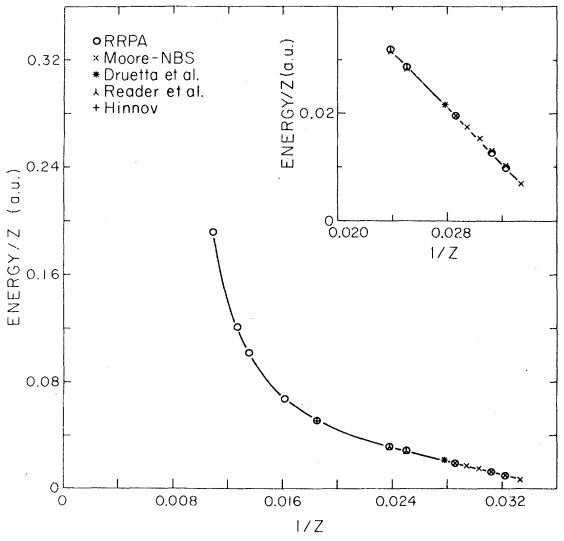

FIG. 1. 4^1S_0-$4\ {}^1P_1$ excitation energy in a.u., divided by the nuclear charge, as a function of Z^{-1}. Other data points, beginning with Moore, are from Refs. 10, 17, 15, and 16.

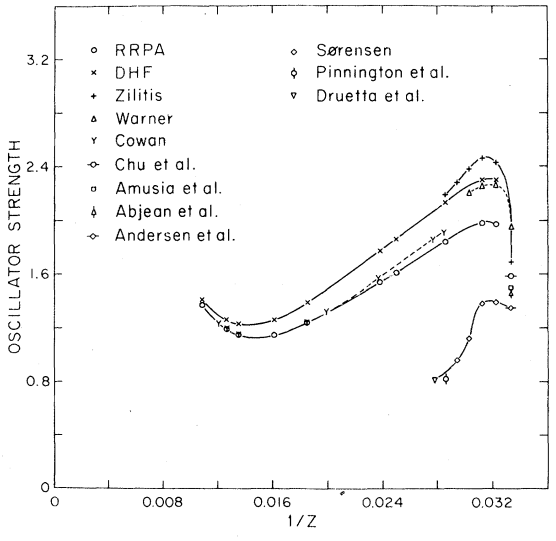

FIG. 2. Oscillator strengths for the 4^1S_0-$4\ {}^1P_1$ transition as a function of inverse nuclear charge. Other data points, beginning with Zilitis, are from Refs. 9, 11, 13, 19, 20, 21, 22, 12, 14, and 17.

TABLE II. RRPA and experimental wavelengths for the $4\,{}^1S_0$-$4,5,6\,{}^1P_1$ resonance transitions.

Z	Ion	Wavelength (Å) $4s4p\,{}^1P_1$	$4s5p\,{}^1P_1$	$4s6p\,{}^1P_1$
31	Ga II	1481	898.6	775.6
		1414[a]	829.6[a]	716.0[a]
32	Ge III	1113	570.8	475.4
		1088[a]	542.6[a]	
35	Br VI	661.7	248.3	195.1
		661.1[a]		
40	Zr XI	396.2	111.6	83.8
		398.4[b]	110.7[c]	
42	Mo XIII	338.9	88.3	65.6
		340.9[b]	87.8[c]	
54	Xe XXV	163.6	32.7	23.5
		164.5[d]		
62	Sm XXXIII	108.6	20.6	14.7
74	W XLV	60.5	11.9	8.4
79	Au L	47.7	9.7	6.9
92	U LXIII	25.8	6.1	4.4

[a] Moore-NBS, Ref. 10.
[b] Reader and Acquista, Ref. 15.
[c] Alexander *et al.*, Ref. 23.
[d] Hinnov, Ref. 16.

data produce a smooth curve which is linear through the region of $Z = 45$. At higher Z relativistic effects steepen the slope. On the scale to which the graph is drawn, the DHF and RRPA results coincide. The inset depicts the linear portion on a larger scale and more clearly illustrates the agreement between theory and experiment.

In the RRPA, we found that despite the neglect of the inner-shell couplings, the length and velocity forms yield oscillator strengths differing by less than 2% whereas the DHF oscillator strengths differ on the average by 8%. The length values are presented in Table I, together with the results of other calculations and experimental measurements.

The various theoretical values are in broad agreement and there is, in particular, close harmony between the RRPA results and those of the HFR method,[18] obtained by Cowan.[13] Agreement generally improves as the nuclear charge increases, as Fig. 2 demonstrates. Figure 2 presents the oscillator strengths as a function of Z^{-1}. The experimental values show a more rapid decrease with increasing ionic charge than do any of the theoretical curves and they are between 30% and 50% smaller than the RRPA results. The frozen-core RRPA oscillator strength of 1.59 for the resonance transition of Zn I, obtained by Chu and Johnson,[19] is in reasonable agreement with the RPA value of 1.50 obtained by Amusia *et al.*,[20] whose calculation included additional correlation effects due to the M-shell electrons. Thus, it seems unlikely that inner-shell core polarization which was ignored in this application of the RRPA can account for the discrepancies.

Tables II and III present the results for the $5\,{}^1P_1$ and $6\,{}^1P_1$ resonance transitions. The $5\,{}^1P_1$ RRPA excitation energies are within 8% and 5%, respective-

TABLE III. RRPA excitation energies (in a.u.) and oscillator strengths (length form) for the $4s^2\,{}^1S_0$-$4s5p\,{}^1P_1$ and $4s^2\,{}^1S_0$-$4s6p\,{}^1P_1$ transitions compared with DHF intermediate coupling results. $A/(B)$ denotes $A\times10^B$.

Z	Ion	$4\,{}^1S_0$-$5\,{}^1P_1$ E(RRPA)	E(DHF)	f(RRPA)	f(DHF)	$4\,{}^1S_0$-$6\,{}^1P_1$ E(RRPA)	E(DHF)	f(RRPA)	f(DHF)
31	Ga^{+1}	0.5070	0.5045	3.50(–2)	7.80(–2)	0.5875	0.5863	4.14(–3)	1.86(–2)
32	Ge^{+2}	0.7983	0.7945	1.44(–3)	3.29(–2)	0.9585	0.9568	4.40(–4)	5.53(–3)
35	Br^{+5}	1.8353	1.8296	3.30(–2)	2.27(–4)	2.3356	2.3328	1.88(–2)	1.86(–3)
40	Zr^{+10}	4.0820	4.0751	1.13(–1)	3.87(–2)	5.4350	5.4316	4.46(–2)	2.00(–2)
42	Mo^{+12}	5.1617	5.1546	1.36(–1)	5.82(–2)	6.9489	6.9454	5.11(–2)	2.68(–2)
54	Xe^{+24}	13.9128	13.9051	2.02(–1)	1.34(–1)	19.3845	19.3807	6.90(–2)	5.05(–2)
62	Sm^{+32}	22.0898	22.0819	2.07(–1)	1.50(–1)	31.0408	31.0369	7.09(–2)	5.56(–2)
74	W^{+44}	38.4445	38.4362	1.84(–1)	1.42(–1)	54.1707	54.1667	6.53(–2)	5.38(–2)
79	Au^{+49}	46.9377	46.9292	1.66(–1)	1.30(–1)	66.0489	66.0448	6.07(–2)	5.04(–2)
92	U^{+62}	74.7796	74.7705	1.06(–1)	8.28(–2)	104.2863	104.2819	4.34(–2)	3.62(–2)

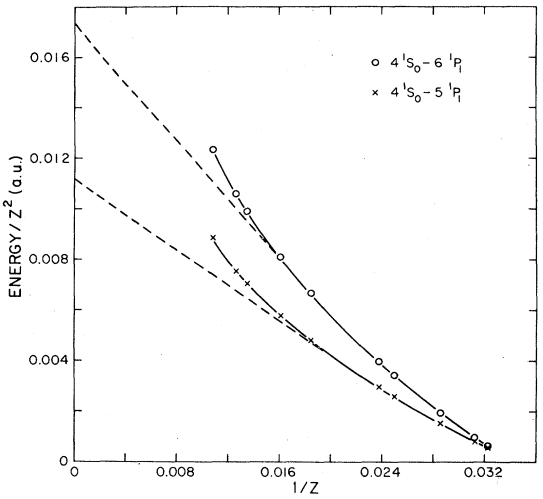

FIG. 3. RRPA excitation energy in a.u., divided by the square of the nuclear charge, as a function of Z^{-1} for the 4 $^1S_0$-5 $^1P_1$ and 4 $^1S_0$-6 $^1P_1$ transitions.

ly of the values given by Moore[10] for Ga II and Ge III and are within 1% of the Zr XI and Mo XIII values of Alexander *et al.*[23] Only the length form of the oscillator strength is tabulated. For both the 5 $^1P_1$ and 6 $^1P_1$ transitions, the difference between the two forms of the RRPA oscillator strengths is less than 1% from Zr^{+10} onward, whereas the difference between the two forms for the DHF results is substantial throughout the sequence. The differences between the RRPA and DHF oscillator strengths are large, especially near the neutral end of the sequence.

Figure 3 depicts the transition energy divided by the square of the nuclear charge as a function of Z^{-1} for the 4 $^1S_0$-5 $^1P_1$ and 4 $^1S_0$-6 $^1P_1$ transitions. The data points have a smooth Z^{-1} dependence. Extrapolation of the curves based on their behavior near $Z = 55$ is in accord with the hydrogenic limits of 0.0113 and 0.0174 a.u. for the 5 $^1P_1$ and 6 $^1P_1$ transitions, respectively.

The oscillator strengths for the transitions are presented as a function of Z^{-1} in Fig. 4. The figure demonstrates the closeness of the RRPA length and velocity results and the discrepancies between the DHF length and velocity results. The oscillator strengths pass through a minimum near the neutral end of the sequence. Thus, because of cancellation in the transition matrix, the theoretical values of the oscillator strengths for the 5 $^1P_1$ and 6 $^1P_1$ transitions of Ge III, As IV, and neighboring elements are very sensitive to small changes in the wave function and some loss of accuracy occurs.

The tabulated oscillator strengths can be converted into transition probabilities using the formula

$$A_{ki}(\text{sec}^{-1}) = 3.213 \times 10^{10}\ (\Delta E)^2 (g_i/g_k) f_{ik},$$

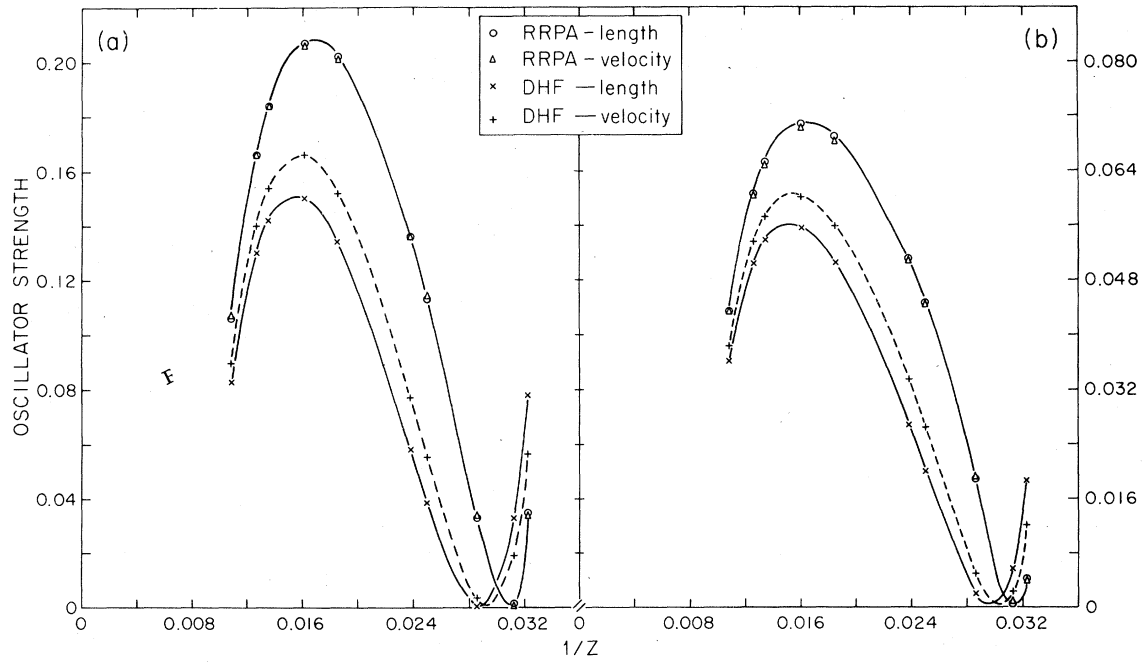

FIG. 4. Oscillator strengths for the (a) 4 $^1S_0$-5 $^1P_1$ and (b) 4 $^1S_0$-6 $^1P_1$ transitions as a function of inverse nuclear charge.

TABLE IV. RRPA transition probabilities, in sec^{-1}. $A(B)$ denotes $A \times 10^B$.

Z	Ion	Transition probabilities $4\,^1P_1$-$4\,^1S_0$	$5\,^1P_1$-$4\,^1S_0$	$6\,^1P_1$-$4\,^1S_0$
31	Ga II	2.00(9)	9.64(7)	1.53(7)
32	Ge III	3.56(9)	9.85(6)	4.33(6)
35	Br VI	9.36(9)	1.19(9)	1.10(9)
40	Zr XI	2.29(10)	2.02(10)	1.41(10)
42	Mo XIII	2.98(10)	3.89(10)	2.64(10)
54	Xe XXV	1.03(11)	4.19(11)	2.78(11)
62	Sm XXXIII	2.17(11)	1.08(12)	7.31(11)
74	W XLV	7.00(11)	2.91(12)	2.05(12)
79	Au L	1.16(12)	3.93(12)	2.83(12)
92	U LXIII	4.55(12)	6.36(12)	5.06(12)

where ΔE is the transition energy in a.u. and g_i and g_k are the statistical weights of the lower and upper states, respectively. Transition probabilities for the $4\,^1P_1$, $5\,^1P_1$, and $6\,^1P_1$ transitions are presented in Table IV.

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