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Relativistic many-body calculations of transition rates for Ca^+, Sr^+, and Ba^+

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Relativistic many-body theory is applied to determine amplitudes for $4p \to 4s$, $4p \to 3d$, and $3d \to 4s$ transitions in Ca^+; $5p \to 5s$, $5p \to 4d$, and $4d \to 5s$ transitions in Sr^+; and $6p \to 6s$, $6p \to 5d$, and $5d \to 6s$ transitions in Ba^+. The calculations, which are carried out through third order in perturbation theory, give lifetimes for excited p states that agree with measured values to better than 10%. The agreement improves to the 2% level after semiempirical corrections are included. The lifetimes predicted for the metastable $4d_{3/2}$ and $4d_{5/2}$ states in Sr^+ and for the $5d_{5/2}$ state in Ba^+ also agree well with measurement, but the theoretical lifetime of the $5d_{3/2}$ state in Ba^+ is a factor of 4 larger than the measured lifetime.

I. INTRODUCTION

In the present paper, relativistic many-body perturbation theory (MBPT) calculations of the lifetimes of low-lying excited states of the alkaline-earth-metal ions Ca^+, Sr^+, and Ba^+ are compared with accurate experimental lifetimes as a test of the quality of theoretical methods for atomic systems with high nuclear charge. The lifetime of the $6p_{3/2}$ state of Ba^+ [1], which has been measured to 0.3% accuracy, provides an especially valuable comparison standard. Lifetimes of the $6p_{1/2}$ state of Ba^+ [2], the $5p_{1/2}$ and $5p_{3/2}$ states of Sr^+ [2], and the $4p_{1/2}$ and $4p_{3/2}$ states of Ca^+ [3], all of which have been measured to 1% accuracy, provide other useful comparison values. We carry out MBPT calculations through third order for the amplitudes of $p \to s$ and $p \to d$ transitions in the three alkaline-earth-metal ions, Ca^+, Sr^+, and Ba^+. From these calculations, we can predict lifetimes of the lowest excited $p_{1/2}$ and $p_{3/2}$ states for each ion. Following the standard prescription of MBPT [4], we obtain theoretical values for the lifetimes of the excited p states that agree with experimental lifetimes to better than 10%.

It has been shown in theoretical studies of the $6p \to 6s$ transition amplitudes in cesium [5], that a semiempirical correction, in which the valence-electron self-energy operator is scaled to give the experimental correlation energy, leads to theoretical lifetimes that agree very closely with precise measurements. We make semiempirical corrections of this type in the present paper, and obtain lifetimes of the excited p states of Ca^+, Sr^+, and Ba^+ that agree with measurement to better than 2%.

The techniques used to study the allowed $E1$ transitions $p \to s$ and $p \to d$ are also used to study the forbidden $E2$ transitions $d \to s$ in the alkaline-earth-metal ions. Here the experimental measurements [6–9], which are made in ion traps, are less precise. Interestingly, we obtain theoretical values that agree well with measurement for the lifetime of the $5d_{5/2}$ state of Ba^+, and for the $4d_{3/2}$ and $4d_{5/2}$ states of Sr^+; but the theoretical lifetime for the $5d_{3/2}$ state of Ba^+ is found to be in serious disagreement with the measured lifetime [9].

Comparisons between *ab initio* calculations and precisely measured atomic properties of heavy atoms are particularly important in view of recent efforts to determine weak-interaction coupling constants from measured parity-nonconserving (PNC) amplitudes [10–12]. Measurements of the $7s \to 6s$ PNC amplitudes in cesium, accurate to 2%, have been made recently [10]. Both experimental and theoretical determinations of PNC amplitudes are needed in order to extract the weak coupling constants from such measurements; the accuracy which can be obtained for the coupling constants is limited by the accuracy of the theoretical transition amplitudes. Indeed, the need for accurate theoretical transition amplitudes to interpret experiments on weak interactions in heavy atoms has been an important stimulant to research on relativistic many-body theory [13–15]. To determine the accuracy of the theoretically calculated PNC amplitudes, one typically calculates amplitudes for allowed transitions and hyperfine constants of low-lying states and compares these with precise experiments. Third-order perturbation theory calculations of allowed transition amplitudes and hyperfine constants in cesium are found to agree with measurements to about 3% [4]; moreover, when the third-order self-energy operator is scaled to give the measured correlation energy, the agreement improves to better than 1% [5].

II. THEORY

Transition amplitudes in the present calculation are evaluated through third order in perturbation theory. The first-order calculations are independent-particle calculations made using Dirac-Hartree-Fock (DHF) wave functions. We solve the DHF equations for the closed ionic core and obtain a frozen-core Hartree-Fock (HF) potential $V_{\rm HF}$. This potential is used to construct a one-electron Hamiltonian $h_{\rm HF}$. The valence DHF equations,

$$h_{\mathrm{HF}}\, v_a = \varepsilon_a v_a, \tag{1}$$

are then solved for the orbitals v_a and eigenvalues ε_a of states of interest. For example, Eq. (1) is solved to give the $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $5d_{3/2}$, and $5d_{5/2}$ states in the case of Ba$^+$. The DHF eigenvalue ε_a is the zeroth-order approximation to the ionization energy of the state a,

$$E_a^{(0)} = \varepsilon_a. \tag{2}$$

Once the valence orbitals have been calculated, the first-order transition amplitudes are found by evaluating the reduced matrix elements of the dipole operator:

$$D_{ba}^{(1)} = \langle v_b \| ez \| v_a \rangle. \tag{3}$$

Second-order calculations give the core-polarization corrections to the first-order independent-particle amplitudes. The second-order transition amplitude is given by

$$D_{ba}^{(2)} = \sum_{c,n} \frac{D_{cn}^{(1)}(g_{bnac} - g_{bnca})}{\varepsilon_c - \varepsilon_n - \omega} + \sum_{c,n} \frac{(g_{bcan} - g_{bcna})D_{nc}^{(1)}}{\varepsilon_c - \varepsilon_n + \omega}. \tag{4}$$

In Eq. (4), the summation index c extends over all occupied core states and the index n extends over all positive-energy excited states. The quantity ω is the excitation energy $\omega = \varepsilon_b - \varepsilon_a$. The quantities g_{abcd} in Eq. (4) are unsymmetrized two-particle Coulomb matrix elements:

$$g_{abcd} = \iint \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, v_a^\dagger(\mathbf{r}_1) v_c(\mathbf{r}_1)\, v_b^\dagger(\mathbf{r}_2) v_d(\mathbf{r}_2) \times d^3r_1 d^3r_2. \tag{5}$$

We include the higher-order core-polarization corrections associated with the random-phase approximation (RPA) in our second-order amplitude. This is done by replacing the first-order amplitudes $D_{cn}^{(1)}$ and $D_{nc}^{(1)}$ on the right-hand side of Eq. (4) with the corresponding RPA amplitudes D_{cn}^{RPA} and D_{nc}^{RPA} obtained by solving the core RPA equations

$$D_{an}^{\mathrm{RPA}} = D_{an}^{(1)} + \sum_{b,m} \frac{D_{bm}^{\mathrm{RPA}}(g_{amnb} - g_{ambn})}{\varepsilon_b - \varepsilon_m - \omega} + \sum_{b,m} \frac{(g_{abnm} - g_{abmn})D_{mb}^{\mathrm{RPA}}}{\varepsilon_b - \varepsilon_m + \omega}, \tag{6}$$

$$D_{na}^{\mathrm{RPA}} = D_{na}^{(1)} + \sum_{b,m} \frac{D_{bm}^{\mathrm{RPA}}(g_{nmab} - g_{nmba})}{\varepsilon_b - \varepsilon_m - \omega} + \sum_{b,m} \frac{(g_{nbam} - g_{nbma})D_{mb}^{\mathrm{RPA}}}{\varepsilon_b - \varepsilon_m + \omega}. \tag{7}$$

The present third-order corrections include only the dominant Brueckner-orbital terms. Third-order RPA terms are already included in the second-order amplitude, and the much smaller [4, 5] third-order structural radiation and normalization corrections are omitted in the present calculation. The third-order Brueckner-orbital corrections δv_a to the valence orbital v_a are found by solving the inhomogeneous Dirac equation

$$(h_{\mathrm{HF}} - \varepsilon_a)\delta v_a = (E_a^{(2)} - \Sigma_{\varepsilon_a}^{(2)})v_a, \tag{8}$$

where $\Sigma_\varepsilon^{(2)}$ is the second-order self-energy operator and $E_a^{(2)}$ is the second-order correction to the ionization energy of the state a. Equation (8) has a nontrivial solution since

$$E_a^{(2)} = \langle v_a | \Sigma_{\varepsilon_a}^{(2)} | v_a \rangle. \tag{9}$$

The physically acceptable solution to Eq. (8) is orthogonal to v_a. Once the Brueckner-orbital corrections δv_a are determined by solving Eq. (8) for the states of interest, the corresponding third-order corrections to the transition amplitudes $D_{ba}^{(3)}$ are given by

$$D_{ba}^{(3)} = \langle \delta v_b \| ez \| v_a \rangle + \langle v_b \| ez \| \delta v_a \rangle. \tag{10}$$

The theoretical amplitude obtained from third-order MBPT, D_{ba}^{theor}, is just the sum of the three terms discussed above,

$$D_{ba}^{\mathrm{theor}} = D_{ba}^{(1)} + D_{ba}^{(2)} + D_{ba}^{(3)}. \tag{11}$$

III. RESULTS OF CALCULATION

Ionization energies of the five states for each of the ions considered are listed in Table I. In the third column of the table we give the lowest-order DHF energies $E^{(0)}$; in the fourth column, we give the second-order correlation energy $E^{(2)}$; in the fifth column we give the corrected theoretical energy $E^{\mathrm{theor}} = E^{(0)} + E^{(2)}$; and in the sixth column, we give the experimental ionization energy. For all states considered, the second-order correlation energy is seen to be too large. In the final column of the table, we give the factor by which one must multiply $E^{(2)}$ (or the self-energy operator $\Sigma_{\varepsilon_a}^{(2)}$) in order that the second-order correlation energy agrees exactly with the experimental correlation energy $E^{\mathrm{expt}} - E^{(0)}$. This scale factor is used below to adjust the correlation corrections to transition amplitudes.

In Table II, we present amplitudes and rates for the $E1$ transitions from the lowest p states of each of the three ions. In the third column of the table, we give the first-order DHF amplitudes $D^{(1)}$; and in the fourth column, we give the MBPT amplitudes D^{theor}, determined from Eq. (11). In the fifth column of Table II, we present semiempirical amplitudes D^{SE} obtained using scaled Brueckner orbitals. To calculate these semiempirical amplitudes, we make two major changes to the MBPT scheme described above.

(i) We include a class of higher-order corrections to the transition amplitudes by interchanging the second- and third-order calculations. To accomplish this interchange, the Brueckner orbitals are first calculated for each valence state a, and corrected valence orbitals w_a, given by

TABLE I. Theoretical and experimental energies (a.u.) for alkaline-earth-metal ions.

Ion	State	$E^{(0)}$	$E^{(2)}$	$E^{\rm theor}$	$E^{\rm expt}$	Scale factor
Ba$^+$	$6s_{1/2}$	−0.343 27	−0.029 80	−0.373 08	−0.367 64	0.8178
	$5d_{3/2}$	−0.310 46	−0.041 26	−0.351 72	−0.345 43	0.8476
	$5d_{5/2}$	−0.308 30	−0.039 18	−0.347 48	−0.341 78	0.8545
	$6p_{1/2}$	−0.260 92	−0.016 50	−0.277 42	−0.275 32	0.8727
	$6p_{3/2}$	−0.254 58	−0.014 88	−0.269 46	−0.267 62	0.8763
Sr$^+$	$5s_{1/2}$	−0.382 92	−0.025 46	−0.408 39	−0.405 35	0.8810
	$4d_{3/2}$	−0.307 03	−0.035 76	−0.342 79	−0.339 03	0.8949
	$4d_{5/2}$	−0.306 38	−0.034 94	−0.341 32	−0.337 75	0.8978
	$5p_{1/2}$	−0.284 83	−0.013 55	−0.298 38	−0.297 30	0.9203
	$5p_{3/2}$	−0.281 71	−0.012 93	−0.294 63	−0.293 65	0.9234
Ca$^+$	$6s_{1/2}$	−0.416 63	−0.021 73	−0.438 36	−0.436 26	0.9034
	$5d_{3/2}$	−0.330 87	−0.046 81	−0.377 68	−0.374 07	0.9229
	$5d_{5/2}$	−0.330 76	−0.046 55	−0.377 31	−0.373 79	0.9244
	$5p_{1/2}$	−0.310 00	−0.012 17	−0.322 17	−0.321 48	0.9433
	$5p_{3/2}$	−0.309 09	−0.012 02	−0.321 11	−0.320 46	0.9459

$$w_a = \sqrt{1-\lambda}\, v_a + \delta v_a, \qquad (12)$$

$$\lambda = \int d^3r\, \delta v_a^\dagger(\mathbf{r}) \delta v_a(\mathbf{r}), \qquad (13)$$

are constructed. We use the corrected valence orbitals w_a rather than DHF orbitals v_a to obtain a modified first-order amplitude

$$\tilde{D}^{(1)}_{ba} = \langle w_b || ez || w_a \rangle, \qquad (14)$$

which is approximately the sum of $D^{(1)}_{ba}$ and $D^{(3)}_{ba}$. Corrected orbitals for the valence states a and b are also used instead of DHF orbitals in Eq. (4) to obtain a modified second-order amplitude $\tilde{D}^{(2)}_{ba}$. The amplitudes $D^{(1)}_{cn}$ and $D^{(1)}_{nc}$ on the right-hand side of Eq. (4) are replaced by RPA amplitudes as described previously. The modified second-order amplitudes determined in this way include the fourth- and higher-order terms arising from interference between the RPA and Brueckner-orbital corrections.

(ii) The second-order self-energy operator (and consequently the second-order energy) is scaled by the factor given in the sixth column of Table I to give the experimental correlation energy. This energy scaling causes the Brueckner orbitals, which are determined from Eq. (8), to be scaled by precisely the same factor. These scaled Brueckner orbitals are then used to calculate the modified amplitudes $\tilde{D}^{(1)}_{ba}$ and $\tilde{D}^{(2)}_{ba}$ described in the preceding

TABLE II. Electric dipole transition amplitudes (a.u.) and transition rates (10^9 sec^{-1}) for alkaline-earth-metal ions.

Ion	Transition	$D^{(1)}$	$D^{\rm theor}$	$D^{\rm SE}$	$A^{\rm SE}$
Ba$^+$	$6p_{1/2} \to 6s_{1/2}$	3.891	3.273	3.300	0.091 78
	$6p_{1/2} \to 5d_{3/2}$	3.745	2.920	3.009	0.033 42
	$6p_{3/2} \to 6s_{1/2}$	5.478	4.616	4.658	0.116 25
	$6p_{3/2} \to 5d_{3/2}$	1.635	1.270	1.312	0.004 35
	$6p_{3/2} \to 5d_{5/2}$	5.001	3.940	4.057	0.035 95
Sr$^+$	$5p_{1/2} \to 5s_{1/2}$	3.485	3.052	3.060	0.126 51
	$5p_{1/2} \to 4d_{3/2}$	3.729	2.989	3.052	0.007 25
	$5p_{3/2} \to 5s_{1/2}$	4.921	4.313	4.325	0.139 62
	$5p_{3/2} \to 4d_{3/2}$	1.657	1.326	1.355	0.000 92
	$5p_{3/2} \to 4d_{5/2}$	5.003	4.026	4.109	0.007 76
Ca$^+$	$4p_{1/2} \to 4s_{1/2}$	3.201	2.886	2.890	0.135 26
	$4p_{1/2} \to 3d_{3/2}$	3.082	2.315	2.373	0.008 77
	$4p_{3/2} \to 4s_{1/2}$	4.527	4.083	4.088	0.138 95
	$4p_{3/2} \to 3d_{3/2}$	1.376	1.033	1.059	0.000 93
	$4p_{3/2} \to 3d_{5/2}$	4.135	3.108	3.186	0.008 24

TABLE III. Lifetimes of excited np states for alkaline-earth-metal ions.

Ion	State	τ^{SE} (ns)	τ^{expt} (ns)
Ba^+	$6p_{1/2}$	7.99	7.92 ± 0.08[a]
	$6p_{3/2}$	6.39	6.31 ± 0.02[b]
Sr^+	$5p_{1/2}$	7.48	7.47 ± 0.07[a]
	$5p_{3/2}$	6.74	6.69 ± 0.07[a]
Ca^+	$4p_{1/2}$	6.94	6.96 ± 0.18[c]
	$4p_{3/2}$	6.75	6.87 ± 0.18[c]

[a] See Gaillard *et al.*, Ref. [2].
[b] See Andrä, Ref. [1].
[c] See Gosselin, Pinnington, and Ansbacher, Ref. [3].

TABLE IV. Lifetimes of excited $(n-1)d$ states for alkaline-earth-metal ions.

Ion	State	τ^{SE} (s)	τ^{expt} (s)	τ^{other} (s)
Ba^+	$5d_{3/2}$	83.7	17.5 ± 4[a]	45.4[e], 72.1[f]
	$5d_{5/2}$	37.2	47.0 ± 16[b], 32.0 ± 5[c]	19.0[e], 33.2[f]
Sr^+	$4d_{3/2}$	0.454	0.395 ± 0.038[d]	0.257[e]
	$4d_{5/2}$	0.405	0.345 ± 0.033[d]	0.209[e]
Ca^+	$3d_{3/2}$	1.271		0.797[e]
	$3d_{5/2}$	1.236		0.774[e]

[a] See Schneider and Werth, Ref. [9].
[b] See Plumelle *et al.*, Ref. [6].
[c] See Nagourney, Dandberg, and Dehmelt, Ref. [7].
[d] See Gerz, Hilberath, and Werth, Ref. [8].
[e] Warner, Ref. [16].
[f] Garstang and Hill, Ref. [17].

paragraph (i). The resulting semiempirical amplitude

$$D_{ba}^{\mathrm{SE}} = \tilde{D}_{ba}^{(1)} + \tilde{D}_{ba}^{(2)} \tag{15}$$

is given in the fifth column of Table II.

The final column of Table II gives the transition rates A^{SE}, calculated using the semiempirical amplitudes D^{SE} and the measured energies.

In Table III, the lifetimes of the excited $p_{1/2}$ and $p_{3/2}$ states, determined from the semiempirical transition rates given in Table II, are compared with experimental measurements. For the $6p_{3/2}$ state of Ba^+, the experimental lifetime is accurate to 0.3% [1]; for the $6p_{1/2}$ state of Ba^+ and for the $5p_{1/2}$ and $5p_{3/2}$ states of Sr^+, the lifetimes are measured to 1% accuracy [2]; and for the $4p_{1/2}$ and $4p_{3/2}$ states of Ca^+, they are measured to 2.5% accuracy [3]. The largest disparity between the semiempirical and measured lifetimes is found for the $4p_{3/2}$ state of Ca^+, where the difference is 1.8%. These results are consistent with previous many-body calculations of transition rates for cesium [5].

In Table IV, we present the results of MBPT calculations of the lifetime of the metastable $(n-1)d$ states of the alkaline-earth-metal ions. These states decay to the ns ground states by $E2$ emission. The calculation of the $E2$ amplitudes follows the pattern outlined in the preceding paragraphs, replacing the electric dipole operator by the electric quadruple operator. The semiempirical calculations are consistent with the measurements, except for $5d_{3/2}$ state of Ba^+, where the theoretical lifetime is four times larger than the measured lifetime. This large difference cannot be explained by two-photon decay or by $M1$ decay from the $5d_{3/2}$ state; both processes are highly suppressed compared to $E2$ transitions.

In summary, we have obtained theoretical lifetimes of low-lying p states of alkaline-earth-metal ions that agree with precisely measured lifetimes to better than 2% accuracy. These comparisons serve as a measure of the quality of similar theoretical calculations, in cases where benchmark experiments are unavailable. For the metastable $5d_{3/2}$ state of Ba^+, we disagree seriously with experiment, and suggest that the measured lifetime is too small by a factor of about 4.

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