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Transition energies of barium and radium by the relativistic coupled-cluster method

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The relativistic coupled-cluster method is used to calculate ionization potentials and excitation energies of the barium and radium atoms and their monocations. Large basis sets are used, with l up to 5, the Dirac-Fock or Dirac-Fock-Breit orbitals found, and the external 28 electrons of barium or 42 electrons of radium are correlated by the coupled-cluster method with single and double excitations. Good agreement (within a few hundred wave numbers) is obtained for the ionization potentials and low excitation energies (up to 3 eV for Ba, 4 eV for Ra). The Breit interaction has little effect on the excitation energies, but it improves significantly the fine-structure splittings of Ra. Large relativistic effects on the energies are observed, up to 1 eV for barium and 2 eV for radium. The nonrelativistic ground states of Ba$^+$ and Ra$^+$ are $(n-1)d\ ^2D$ rather than $ns\ ^2S$.

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I. INTRODUCTION

Several calculations of ionization potentials (IP) and excitation energies (EE) of the barium atom have been reported. Rose *et al.* [1] applied the numerical multiconfiguration Dirac-Fock (MCDF) method [2] to the $6s^2$, $5d6s$, $5d^2$, and $6p^2$ levels. They found very large relativistic effects, which make their inclusion by first-order perturbation theory unreliable. The MCDF results gave moderately good agreement with experiment, with errors of ~2000 cm^{-1} for the lower excitation energies, increasing considerably for the higher levels. Very strong dependence on the configurations included in the MCDF scheme was observed.

Migdałek and Baylis [3] applied MCDF to the ionization potential and $6s^2\ ^1S_0 \rightarrow 6s6p\ ^{1,3}P_1$ excitations. They agreed with experiment to 1500 cm^{-1} in the IP and 700 cm^{-1} in the EE's. In later work [4] they calculated the $5d6s\ ^{1,3}D_2$ states. Their MCDF EE's were 2300–2900 cm^{-1} too high, and the Breit effect reduced them by 50 cm^{-1}. Higher QED effects, calculated in the hydrogenic approximation, amounted to ~2500 cm^{-1}, and brought the calculated energies within a few hundred wave numbers of experiment. This estimate of QED effects seems rather high for a neutral atom, and is out of line with Lindgren's [5] order-of-magnitude estimates. Previous calculations [6,7] gave highly accurate ionization potentials and excitation energies for Cs, agreeing with experiment within 40–120 cm^{-1} without including QED effects. This point is discussed in Sec. IV C below.

Other relevant calculations on Ba include the MCDF work of Kotochigova and Tupizin [8], who shifted their excitation energies to match experimental ionization potentials, and the application of relativistic many-body perturbation theory to Ba$^+$ by Guet and Johnson [9]. We are not aware of comparable calculations for Ra.

Accurate theoretical prediction of transition energies in heavy atoms requires high-order inclusion of both relativistic and correlation terms in the Hamiltonian. An *ab initio* relativistic coupled cluster (RCC) method incorporating both effects has been applied recently to a series of heavy atoms, including gold [10], mercury [11], several lanthanides and actinides [12,13], and elements 104 [14], 111 [15], and 112 [11]. Calculated transition energies were in very good agreement with known experimental values, usually within a few hundred wave numbers. Even higher accuracy was obtained for fine-structure splittings. The method is applied here to atomic barium and radium.

II. METHOD

The relativistic coupled-cluster method has been described in our previous publications [7,10], and only a brief review is given here. We start from the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian [16,17],

$$H_+ = H_0 + V, \tag{1}$$

where (in atomic units)

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+ , \tag{2}$$

$$h_D(i) = c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\text{nuc}}(i) + U(i), \tag{3}$$

$$V = \sum_{i<j} \Lambda_i^+ \Lambda_j^+ (V_{\text{eff}})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+ . \tag{4}$$

Here h_D is the one-electron Dirac Hamiltonian. An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V. This potential is chosen to approximate the effect of the electron-electron interaction and minimize the perturbation; here it is the Dirac-Fock self-consistent-field potential. The nuclear potential V_{nuc} includes the effect of finite nuclear size. Λ_i^+ are projection operators onto the positive energy states of the Dirac Hamiltonian h_D. Because of their presence, the Hamiltonian H_+ has normalizable, bound-state solutions. This approximation is known as the no-(virtual)-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential $V_{\rm eff}$ depends on the gauge used. In Coulomb gauge it becomes (in atomic units, correct to second order in the fine-structure constant α) [18]

$$V_{\rm eff}=\frac{1}{r_{12}}+B_{12}+O(\alpha^3), \tag{5}$$

where the frequency-independent Breit interaction is

$$B_{12}=-\frac{1}{2r_{12}}[\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2+(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})/r_{12}^2]. \tag{6}$$

In q-number theory the Dirac-Coulomb-Breit Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators, $\{r^+s\}$ and $\{r^+s^+ut\}$ [16,19]

$$\begin{aligned}H&=H_+-\langle 0|H_+|0\rangle\\&=\sum_{rs} f_{rs}\{r^+s\}+\frac{1}{4}\sum_{rstu}\langle rs||tu\rangle\{r^+s^+ut\},\end{aligned} \tag{7}$$

where f_{rs} and $\langle rs||tu\rangle$ are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb-Breit interaction matrices over Dirac four-component spinors. The effect of the projection operators Λ^+ is now taken over by the normal ordering, denoted by the curly brackets in the equation above, which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive energy state, and the negative energy states are ignored.

The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic open-shell CC theory. The multireference valence-universal Fock space coupled-cluster approach is employed here, which defines and calculates an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. According to Lindgren's formulation of the open-shell CC method [20], the effective Hamiltonian has the form

$$H_{\rm eff}=PH\Omega P, \tag{8}$$

where Ω is the normal-ordered wave operator,

$$\Omega=\{\exp(S)\}. \tag{9}$$

The excitation operator S is defined in the Fock-space coupled-cluster approach with respect to a closed-shell reference determinant. In addition to the traditional decomposition into terms with different total (l) number of excited electrons, S is partitioned according to the number of valence holes (m) and valence particles (n) to be excited with respect to the reference determinant,

$$S=\sum_{m\geqslant 0}\sum_{n\geqslant 0}\left(\sum_{l\geqslant m+n} S_l^{(m,n)}\right). \tag{10}$$

The upper indices in the excitation amplitudes reflect the partitioning of the Fock space into sectors, which correspond to the different numbers of electrons in the physical system. This partitioning allows for partial decoupling of the open shell CC equations, since the equations in each sector do not involve excitation amplitudes from higher sectors. The eigenvalues of the effective Hamiltonian (8) in a sector give directly the correlated energies in that sector with respect to the correlated (0,0) reference state. These transition energies may be ionization potentials, electron affinities, or excitation energies, according to the presence of valence holes and/or valence particles.

In the present application, we use the (0,0), (0,1), and (0,2) sectors. The lower index l in (10) is truncated at $l=2$. The resulting coupled cluster with single and double excitations (CCSD) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes, and sums all diagrams with these excitations to infinite order. Negative energy states are excluded from the Q space, and the diagrammatic summations in the CC equations are carried out only within the subspace of the positive energy branch of the Dirac-Fock spectrum.

III. CALCULATIONS

The Fock-space relativistic coupled-cluster method was applied to several ionization states of the barium and radium. Starting from the closed-shell M^{2+} ions, two electrons were added, one at a time, according to the sequence

$$M^{2+}(0,0)\rightarrow M^+(0,1)\rightarrow M(0,2). \tag{11}$$

The Dirac-Fock [19] and RCC [7,10] programs are both written for spherical symmetry, utilizing the angular decomposition of the wave function and CC equations in a central field. The energy integrals and CC amplitudes which appear in the Goldstone-type diagrams defining the CC equations are decomposed in terms of vector-coupling coefficients, expressed by angular-momentum diagrams, and reduced Coulomb-Breit or S matrix elements, respectively. The reduced equations for single and double excitation amplitudes are derived using the Jucys-Levinson-Vanagas theorem [20] and solved iteratively. This technique makes possible the use of larger basis sets.

To avoid "variational collapse" [21], the Gaussian spinors in the basis are made to satisfy kinetic balance [22]. They also satisfy relativistic boundary conditions associated with a finite nucleus, described here as a sphere of uniform proton charge [19]. The atomic masses used are 137.34 for Ba and 226 for Ra. The speed of light c is 137.035 99 atomic units. Nonrelativistic calculations are carried out by setting c to 10^5 a.u.

The uncontracted well-tempered basis set of Huzinaga and Klobukowski [23] was used for Ba, and the universal basis set of Malli *et al.* [24] was selected for Ra. The basis sets, which go up to h orbitals ($l=5$), are summarized in Table I. Atomic orbitals with the same l but different k number (e.g., $p_{1/2}$ and $p_{3/2}$) are expanded in the same basis functions. Virtual orbitals with high orbital energies have been found in previous applications to contribute very little to correlation effects on excitation energies; orbitals higher than 100 a.u., which correlate low-lying inner-shell electrons, are therefore eliminated from the calculation, effecting considerable savings in computational effort.

As described above, we start from the closed-shell dication. For barium, the $4spd5sp$ electrons of Ba^{2+} are corre-

TABLE I. Basis sets for Ba and Ra. Members of the well- or even-tempered s-basis series used in the various l sectors are given.

	Basis	Ref.	s	p	d	f	g	h
Ba	$31s26p22d17f13g8h$	[23]	1–31	5–30	8–29	11–27	14–26	17–24
Ra	$34s25p21d15f10g6h$	[24]	1–34	9–33	13–33	17–31	21–30	24–29

lated, and two electrons are added, one at a time, in the $6s$, $6p$, and $5d$ shells, recorrelating the whole system at each step. A similar procedure is followed for the radium atom, where the $4f5spd6sp$ electrons are correlated and electrons are added in $7s$, $7p$, and $6d$. The iterative solution of the coupled-cluster equations converged rapidly in the (0,0) and (0,1) sectors, but convergence difficulties arose in the (0,2) sector. Convergence of the coupled-cluster equations depends on a clear separation of the determinants into P and Q spaces, with a P-Q energy gap large relative to the energy span of P-space determinants; otherwise, so-called ‘‘intruder states’’ appear and spoil the convergence [25,26]. No such separation can be achieved here if a complete model space (consisting of all two-electron combinations of the valence orbitals) is used. We resorted therefore to the incomplete model space scheme [25,27], leaving the $6p^2$ configuration out of the P space. Even with the help of the incomplete model space, convergence was not easy. Damping and reduced linear equations [28] were used, but it still took 45 iterations to converge all excitation amplitudes to 10^{-6}. Radium was even more difficult: both the $5d^2$ and $6p^2$ configurations had to be relegated to Q space, and 84 iterations were required for convergence. All computations were carried out on the IBM RS6000/320 and 390 workstations at Tel Aviv University.

TABLE II. Ionization potential (IP) and excitation energies (EE) of Ba^+ and Ba (cm^{-1}).

State			Expt [29,30].	Present work	Other calculations	
			Ba^+, ground state $6s\ {}^1S_{1/2}$			
IP			80687	80871	81882 [9]	
EE	$5d$	${}^2D_{3/2}$	4874	5268	4688 [9]	
		${}^2D_{5/2}$	5675	6093	5620 [9]	
	$6p$	${}^2P_{1/2}$	20262	20396	20995 [9]	
		${}^2P_{3/2}$	21952	22103	22742 [9]	
			Ba, ground state $6s^2\ {}^1S_0$			
IP			42032	42967	40572 [3]	
EE	$5d6s$	${}^3D_1$	9034	9241	11164 [1]	
		${}^3D_2$	9216	9429	11280 [1]	12126 [4]
		${}^3D_3$	9597	9818	11492 [1]	
		${}^1D_2$	11395	11841	13164 [1]	13677 [4]
	$6s6p$	${}^3P_0$	12226	12503		
		${}^3P_1$	12637	12882	11902 [3]	
		${}^3P_2$	13515	13792		
		${}^1P_1$	18060	18455	17393 [3]	
	$5d^2$	${}^3F_2$	20934	21334	23570 [1]	
		${}^3F_3$	21250	21663	23710 [1]	
		${}^3F_4$	21624	22060	23894 [1]	
	$5d6p$	${}^3F_2$	22062	22705		
		${}^3F_3$	22947	23632		
		${}^3F_4$	23757	24491		
		${}^1D_2$	23074	23823		
	$5d^2$	${}^1D_2$	23062	24256	25427 [1]	
		${}^3P_0$	23209	24218	24435 [1]	
		${}^3P_1$	23480	24427	24703 [1]	
		${}^3P_2$	23919	24943	24867 [1]	
		${}^1G_4$	24300±300	25585	29435 [1]	
	$5d6p$	${}^3D_1$	24192	25502		
		${}^3D_2$	24532	25835		
		${}^3D_3$	24980	26321		
		${}^3P_0$	25642	27151		
		${}^3P_1$	25704	27204		
		${}^3P_2$	25957	27391		

TABLE III. Dirac-Coulomb (DC) and nonrelativistic (NR) term energies of Ba (cm^{-1}).

State			Expt [29].	DC	NR
		Ba$^+$, ground state $6s$ ^2S			
IP			80687	80870	78180
EE	$5d$	^2D	5355	5764	-259
	$6p$	^2P	21389	21535	19101
		Ba, ground state $6s^2$ ^1S			
IP			42032	42965	41251
EE	$5d6s$	^3D	9357	9614	4946
		^1D	11395	11841	6640
	$6s6p$	^3P	13079	13353	11586
		^1P	18060	18459	15389
	$5d^2$	^3F	21335	21808	13169
		^1D	23062	24239	16609
	$5d6p$	^1D	23074	23848	17015
		^3F	23084	23819	17497
	$5d^2$	^3P	23694	24756	16439
		^1G		25759	17451
	$5d6p$	^3D	24673	26072	19214
		^3P	25838	27383	20900

IV. RESULTS AND DISCUSSION

A. Ba

The calculated ionization potentials and excitation energies of barium and its cation are shown in Table II and compared with experiment [29,30] and with previous calculations [1,3,4,9]. The RCC results are more accurate than any previously reported. The calculated excitation energies are generally higher than experiment. The errors start at 200–400 cm^{-1} (0.025–0.05 eV) for the low excitations, and in-

TABLE IV. Ionization potential (IP) and excitation energies (EE) of Ra$^+$ and Ra (cm^{-1}).

State			Expt [29].	DC	DCB
		Ra$^+$, ground state $7s$ $^1S_{1/2}$			
IP			81842	82043	82025
EE	$6d$	$^2D_{3/2}$	12084	12507	12429
		$^2D_{5/2}$	13743	14192	14089
	$7p$	$^2P_{1/2}$	21351	21527	21563
		$^2P_{3/2}$	26209	26400	26396
		Ra, ground state $7s^2$ $^1S_0$			
IP			42577	43310	43303
EE	$7s6d$	$^3D_1$	13716	13672	13609
		$^3D_2$	13994	13974	13907
		$^3D_3$	14707	14715	14636
		$^1D_2$	17081	17806	17737
	$7s7p$	$^3P_0$	13078	13136	13166
		$^3P_1$	13999	14072	14096
		$^3P_2$	16689	16855	16855
		$^1P_1$	20716	21156	21148
	$6d7p$	$^3F_2$	28038	28341	28306
		$^3F_3$	30118	30570	30513
		$^3F_4$	32368	32941	32860
		$^1D_2$	30918	31484	31416
	$6d7p$	$^3D_1$	32230	32496	32434
		$^3D_2$	32507	33392	33317
		$^3D_3$	33197	34551	34465
		$^3P_0$	33782	34714	34644
		$^3P_1$	33824	34710	34640
		$^3P_2$	34383	35248	35164

TABLE V. Fine-structure splittings in the low levels of Ra (cm^{-1}). Differences between adjacent sublevels are shown.

Level	Expt. [29]	DC	DCB
$7s6d\ ^3D$	278	302	298
	713	741	729
$7s7p\ ^3P$	921	936	930
	2690	2783	2759
$6d7p\ ^3F$	2080	2229	2207
	2250	2371	2347

crease to 1500 cm^{-1} for the highest levels reported. The relativistic effects may be seen in Table III, where experimental term energies (LS averages) are compared with Dirac-Coulomb and nonrelativistic values. The $6s \rightarrow 5d$ excitation energy of Ba^+ is increased relativistically by about 6000 cm^{-1} (0.75 eV), and the $6p$ EE goes up by 2400 cm^{-1} (0.3 eV). This is a manifestation of the well-known differential effect on atomic orbitals, where low-l shells are stabilized relative to orbitals with higher l. The same trend is observed in the levels of the neutral barium atom, where $6s$ to $6p$ excitation energies are augmented relativistically by 2000–3000 cm^{-1}, $6s$ to $5d$ by 5000 cm^{-1}, $6s^2 \rightarrow 5d6p$ by about 7000 cm^{-1}, and $6s^2 \rightarrow 5d^2$ transition energies are increased by 8000 cm^{-1} (1 eV). An interesting observation emerging from Table III is the nature of the nonrelativistic ground state of Ba^+, which turns out to be $5d\ ^2D$ rather than $6s\ ^2S$, although the difference is rather small. The ^2D is, indeed, the ground state of isoelectronic La^{2+}; were it not for relativity, the turnover would have occurred one element earlier, at Ba^+. As it is, the $5d$ orbital plays an important role in the chemical bonding of Ba and neighboring atoms in the Periodic Table [31].

B. Ra

The ionization potentials and excitation energies of Ra^+ and Ra are collected in Table IV. Both Dirac-Coulomb and Dirac-Coulomb-Breit values are given and compared with experiment [29]. Agreement with experiment is better than for Ba, with errors of a few hundred wave numbers for levels up to 4 eV (32 000 cm^{-1}) above ground state. The Breit term (6) has little effect (<100 cm^{-1}) on energy levels. It does improve the fine-structure splittings (see Table V), except for the high ^3D and ^3P levels, where larger errors occur both in excitation energies and splittings.

Relativistic effects are, as expected, larger than for Ba (Table VI). The $7p$ excitation energy of Ra^+ is raised by 7000 cm^{-1} and the $6d$ by 15 000 cm^{-1} upon inclusion of relativity. In neutral radium, the $7s \rightarrow 7p$ energies go up by 5500–7500 cm^{-1}, $7s \rightarrow 6d$ increase by 11 000–13 500 cm^{-1}, and the two-electron excitations to $6d7p$ are pushed up by 13 000–17 000 cm^{-1}. The nonrelativistic ground state of the cation is again $6d\ ^2D$, which is lower than $7s\ ^2S$ by a healthy margin of 1765 cm^{-1}.

C. Sources of error

Several types of approximation are made in the calculations reported here. The first is the truncation of the relativistic Hamiltonian after α^2 terms. Migdałek and Baylis [4] gave estimates of $\sim$2500 cm^{-1} for the effect of the Lamb shift on Ba transition energies. For the neighboring Cs atom, Blundell *et al.* [6] calculated the ionization potential within 120 cm^{-1} of experiment, and a more recent coupled-cluster

TABLE VI. Dirac-Coulomb (DC), Dirac-Coulomb-Breit (DCB), and nonrelativistic (NR) term energies of Ra (cm^{-1}).

	State	Expt [29].	DC	DCB	NR
		Ra^+, ground state $7s\ ^2S$			
IP		81842	82043	82025	74140
EE	$6d\ ^2D$	13079	13518	13425	-1765
	$7p\ ^2P$	24590	24776	24785	17791
		Ra, ground state $7s^2\ ^1S$			
IP		42577	43310	43303	36356
EE	$6d7s\ ^3D$	14271	14259	14188	2960
	^1D	17081	17806	17737	4288
	$7s7p\ ^3P$	15391	15514	15525	10800
	^1P	20716	21156	21148	13629
	$6d7p\ ^3F$	30587	31042	30993	14782
	^1D	30918	31484	31416	14309
	^3D	32274	33754	33676	16278
	^3P	34130	35009	34932	18016
	^1F		36923	36833	19059
	^1P		38060	38012	25143

calculation [7] had an error of 40 cm^{-1}. Both calculations neglected higher QED terms. We have not been able to find calculations of QED effects for heavy neutral atoms; an order-of-magnitude estimate can, however, be made. The tables of Johnson and Soff [32] give the value of 4.3×10^5 cm^{-1} for the 1s electron of Ba^{55+}. More recent calculations [33] yield results of the same order. Since the effect is roughly proportional to the quantum number n^{-3}, [32] it would be about 2000 cm^{-1} for a 6s electron of the one-electron ion, close to the value quoted by Migdałek and Baylis. For a neutral atom, however, the effective charge is much lower than 56; since the Lamb shift is proportional to the fourth power of the nuclear charge, it would be considerably smaller than the Migdałek and Baylis value. Lindgren [5] has estimated that higher QED effects are not necessary for neutral and weakly ionized atoms at the accuracy level of 1% of correlation energy. We therefore believe that the neglect of higher QED effects does not account for the bulk of the errors in the results reported here.

Two other sources of error are the finite size of the basis sets and the truncation of the coupled-cluster expansion (10) at the singles-and-doubles level. Convergence with respect to the basis was examined in detail in previous applications to Pr^{3+} [12] and Rf [14]. It was found there that sets of the type and size used here give ionization potentials and excitation energies converged to a few hundred wave numbers, which is the magnitude of the present errors. The observation that calculated EE's are generally larger than experiment, with the errors increasing for higher excitations, also points to some deficiencies in the basis, since higher orbitals are more difficult to span accurately. Inclusion of triple excitations in the coupled-cluster scheme with basis sets of the size used here is beyond our capability. Blundell *et al.* [6] estimate the effect on the ionization potential of Cs at 0.5–1.0%, or a few hundred wave numbers, which is again the correct order of magnitude.

An interesting observation is that results for Ra are more accurate than for Ba. We do not know the reasons, but note a similar phenomenon in a previous application [12], where excitation energies of U^{4+} were more accurate than those of Pr^{3+}.

V. SUMMARY AND CONCLUSION

Ionization potentials and excitation energies were calculated for barium and radium and their monocations. Good agreement with experiment is obtained for the lower levels (up to about 3 eV for Ba and 4 eV for Ra). Large relativistic effects are observed; the ground state of the cations in the nonrelativistic approximation is $(n-1)d\ ^2D$ rather than the relativistic (and experimental) $ns\ ^2S$. The Breit term, included in the radium calculations, has small effect on excitation energies, but improves considerably the fine-structure splittings.

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