Spectra of barium, radium, and element 120; application of the combined correlation potential, singles-doubles, and configuration interaction \textit{ab initio} method

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We apply a version of the recently developed approach combining the correlation potential, linearized singles-doubles coupled-cluster, and the configuration interaction methods to the spectra of the heavy alkaline earths barium, radium, and element 120. Quantum electrodynamics radiative corrections are included. We have found unprecedented agreement between \textit{ab initio} theory and experiment for the spectra of barium and radium, and we make accurate predictions for missing and unreliable data for all three atoms.

I. INTRODUCTION

Preparatory work with the radium atom towards measurements of fundamental symmetries violations is in progress at Argonne National Laboratory (USA) [1] and Kernfysisch Versneller Institut (The Netherlands) [2]. Studies of the parity and time-reversal violating atomic electric dipole moment (EDM) and atomic parity violation (APV) are particularly attractive in radium due to orders of magnitude enhancement of the effects, arising from both nuclear and electronic mechanisms: the presence of octupole deformation of the nucleus may lead to several-hundred times nuclear enhancement of the EDM in radium in the electronic ground state compared to mercury (see, e.g., [3, 4]), for which the best limit on an atomic EDM has been placed [5]; the presence of anomalously close electronic levels of opposite parity may lead to orders of magnitude electronic enhancement of EDM effects in metastable states and APV effects in certain transitions [6, 7].

High-precision atomic structure calculations will be required for interpretation of the APV and atomic EDM measurements [8]. Moreover, the measured low-lying excitation energies for radium are incomplete, and it is important to have high-precision predictions for these levels. There are already a number of theoretical works devoted to studies of fundamental symmetries violations in radium [6, 9–14] and to the radium spectra, lifetimes, and hyperfine structure [15–21]. There are also recent measurements of a few transition frequencies and lifetimes [22–24]. In this work we use a recently-developed approach that combines the correlation potential, singles-doubles coupled-cluster, and configuration interaction methods [25] to the radium spectra. We have found unprecedented agreement between theory and experiment for most levels using this \textit{ab initio} method.

The heavier electronic homologue of radium is element 120. Efforts to synthesize this element are underway at GSI (Germany), JINR (Russia), and RIKEN (Japan) (see, e.g., [26]). This element lies within the predicted island of stability, a region of increased stability against nuclear decay close to the next doubly magic shell closures $Z=114$, 120, or 126 and $N=172$ or 184, depending on the model [24]. If $Z=120$ is the next closed proton shell, significantly increased stability is expected for this element. Enhanced stability could make atomic and chemical studies of this element possible. Already, chemical studies involving the superheavy element Sb ($Z=106$) have proved successful [28]. The current calculations for E120 extend the spectral range considered in previous works [24, 31].

We also perform calculations for the lighter electronic homologue barium, as this can be used to gauge the accuracy for the heavier elements. The method used in this work has already been applied to the low-lying levels of barium in Ref. [25]. Here we extend the application to the excitation energies of the lowest 31 levels.

II. METHOD OF CALCULATION

We use an approach that is based on the combination of several different many-body methods: the correlation potential (CP), linearized singles-doubles coupled-cluster (SD), and configuration interaction (CI) methods. It may be referred to as the CP+SD+CI method. This method was recently developed by Dzuba in Ref. [32] and is similar to the combined SD+CI method developed by Safronova et al. [32].

The CP+SD+CI and SD+CI methods are essentially based on the method combining many-body perturbation theory and the configuration interaction (MBPT+CI) [33], which has proven to be one of the most computationally efficient and accurate approaches for calculations involving heavy atoms with several valence electrons. These methods differ in their treatment of the valence-core correlations and the screened Coulomb interaction (valence-core-valence correlations), as we explain below.

Barium, radium, and element 120 have two valence electrons above a closed electronic core. We wish to find the eigenvalues and eigenvectors of the effective Hamiltonian for the two valence electrons,

$$H^{CI} = h_1(r_1) + h_1(r_2) + h_2(r_1, r_2),$$

by diagonalizing $H^{CI}$ with respect to wavefunctions constructed from linear combinations of two-electron Slater determinants; the Slater determinants are formed from...
TABLE I. Factors for Ba used to mimic higher-order screening for exchange diagrams, \( f_k = \langle v | \Sigma_{\text{dir},k}^{(2)} | v \rangle / \langle v | \Sigma_{\text{dir},k}^{(2)} | v \rangle \) and \( f_k^{hp} = \langle v | \Sigma_{\text{dir},k}^{(2)} | v \rangle / \langle v | \Sigma_{\text{dir},k}^{(2)} | v \rangle ; k \) is the multipolarity of the Coulomb interaction.

| \( k \) | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  |
|-----|----|----|----|----|----|----|----|----|----|----|
| \( f_k \) | 0.73 | 0.61 | 0.83 | 0.91 | 0.99 | 1.05 | 1.10 | 1.00 | 1.00 | 1.00 |
| \( f_k^{hp} \) | 0.86 | 0.73 | 0.97 | 1.02 | 1.07 | 1.11 | 1.15 | 1.00 | 1.00 | 1.00 |

In the MBPT+CI method, both \( \Sigma_1 \) and \( \Sigma_2 \) are calculated using MBPT; they are often calculated in only second-order in the Coulomb interaction. We have demonstrated before, that using the all-order correlation potential \( \Sigma_{1\infty} \) in place of the second-order correlation potential \( \Sigma_1^{(2)} \) leads to significantly improved accuracy \[19\]. We refer to this latter approach, with the all-order \( \Sigma_1^{\infty} \), as the CP+CI method. In the SD+CI method \[32\], both \( \Sigma_1 \) and \( \Sigma_2 \) are found from all-order linearized singles-doubles coupled-cluster equations.

In the current CP+SD+CI approach, we calculate the all-order \( \Sigma_1^{\infty} \) using the Feynman diagram technique, while the screening of the Coulomb interaction \( \Sigma_2 \) is found from the SD method. In this way, we include important classes of many-body diagrams to all-orders in the Coulomb interaction, both for \( \Sigma_1 \) and \( \Sigma_2 \). It was shown in Ref. \[23\] that high accuracy in excitation energies can be obtained with this choice.

In the calculation of \( \Sigma_1 \), the Feynman diagram technique is used to include two classes of diagrams to all orders in the Coulomb interaction for the direct part: the electron-electron Coulomb screening and the hole-particle interaction inside the internal loops \[34\]. The exchange part is evaluated in second-order in the Coulomb interaction by calculation of the corresponding Goldstone diagrams. Screening is taken into account in a simplified way, by multiplying the Coulomb integrals by factors found from the direct diagrams (more on this below). There is another series of diagrams, referred to as “ladder diagrams”, that are calculated using singles-doubles-type equations \[35\]; the corresponding corrections to the valence energies are added to the CI matrix.

Screening factors for the exchange diagrams are found by taking the ratio of the expectation value for the direct part of \( \Sigma_{1\infty,\text{ee}} \) (with the dominant all-orders electron-electron screening considered) to the expectation value for the direct part of \( \Sigma_1^{(2)} \) for each multipolarity \( k \), that is, \( f_k = \langle v | \Sigma_{\text{dir},k}^{\infty,\text{ee}} | v \rangle / \langle v | \Sigma_{\text{dir},k}^{(2)} | v \rangle \). The corresponding factors for Ba are shown in the first row of Table I. Later, as a test of our accuracy, we consider the effect of using a different set of screening factors \( f_k^{hp} \), found by considering both the dominant electron-electron screening and the hole-particle interaction series of diagrams; these factors are listed in the second row of Table I.

Note that we used slightly different factors for \( f_k \) in different approximations (with or without Breit or QED corrections) as well as slightly different factors for different atoms (Ba, Ra, E120). They differ by a few percent at most, and as their precise values are not of general interest, we do not present them here.

We refer the reader to Ref. \[25\] for details regarding the calculation of \( \Sigma_2 \).

In this work we quantify the corrections associated with inclusion of the Breit interaction and the quantum electrodynamics radiative corrections. The Breit interaction is considered at the relativistic Hartree-Fock (RHF) level. The radiative corrections are taken into account through the addition of a local radiative potential \[36\] to the nuclear potential. This radiative potential method provided a breakthrough in the ability for radiative corrections to be included into the many-body problem in heavy atoms. We refer the reader to Ref. \[36\] for details about this method. The radiative potential method has since been implemented in a number of works, including (with a minor modification to one of the fitting factors in the radiative potential) Refs. \[37, 38\], where the radiative potential was added to the atomic many-body package GRASP \[39, 40\].

The upper and lower radial components of the relativistic Hartree-Fock orbitals in the \( V^{N-2} \) potential are expanded in a basis of B-splines of order \( k = 9 \) \[41\]. We use 40 B-splines for Ba and Ra and 50 B-splines for E120 confined to a cavity of radius 40 a.u. We perform the calculations for the exchange part of the correlation potential, the ladder diagrams, and \( \Sigma_2 \) using the lowest 30 states in each partial wave up to \( l = 6 \) for the intermediate excitations. We include the correlation potential \( \Sigma_1 \) for the valence levels up to \( l = 4 \) and \( \Sigma_2 \) for the valence levels up to \( l = 3 \). At the CI stage of the calculations,
with higher angular momenta.

logues, which in turn screen and push out the orbitals

E120

all

for each of these runs. For each run, one basis is used for
tions enter at this level, we have used a different basis set
by the Hartree-Fock orbitals, and Breit and QED correc-
both Breit and QED. As the basis is determined
with both Breit and QED. As the basis is determined

we perform the RHF calculations in the field of the
electrons of the core. Therefore, the quality of the spec-
tal" in Tables II, III, IV the effect of the relativistic con-

We have carried out three runs of the calculations, for
each run, one basis is used for
all aspects of the many-body problem: CP, SD, and CI.

III. RESULTS

Our calculations begin for the ions Ba\(^+\), Ra\(^+\), and E120\(^+\). The correlation potential \(\Sigma_1\) that describes the valence-core correlations is the same for the monovalent ions above as for the divalent atoms Ba, Ra, E120 when we perform the RHF calculations in the field of the \(N-2\) electrons of the core. Therefore, the quality of the spectra for the ions is a good indication of the quality of the correlation potential \(\Sigma_1\).

A. Ions

Results for the ionization energies of the lowest partial waves up to \(l = 3\) for the ions Ba\(^+\), Ra\(^+\), and E120\(^+\) are presented in Tables II, III, and IV respectively. We separate the contributions arising from inclusion of the correlation potential \(\Sigma_1^{\infty}\) (without ladder diagrams), ladder diagrams “Lad.”, the Breit interaction, and QED radiative corrections.

Absolute differences of our final results from experiment are listed in the last column under “\(\Delta\)”. These differences for Ba\(^+\) and Ra\(^+\) are very small, on the order of \(10-100\) cm\(^{-1}\), with the largest difference \(|\Delta| \approx 160\) cm\(^{-1}\). We expect a similar level of agreement for E120\(^+\).

We can see from a comparison of the final results “Total” in Tables II, III, IV the effect of the relativistic contraction of the \(s\) and \(p_{1/2}\) orbitals in the heavier homologues, which in turn screen and push out the orbitals with higher angular momenta.

Inclusion of the ladder diagrams is very important for reaching good agreement for the \(d\) levels. The \(d\)-orbitals are very low-lying in the ions and play a big role in the low-lying spectra of the neutral divalent atoms. The size of the ladder diagram contribution decreases as we go from Ba\(^+\) to E120\(^+\), as the \(d\) orbitals are pushed out, while the contributions for \(s\) and \(p\) levels increase.

The contributions from Breit and QED are roughly of the same magnitude, and generally increase with higher \(Z\). The QED corrections exceed 100 cm\(^{-1}\) for the \(s\) levels for E120\(^+\), while they are negligible for the \(p\) waves. The largest Breit corrections we see are for the \(f\) levels, almost reaching 200 cm\(^{-1}\). Interestingly, these \(f\)-wave corrections are mostly determined by many-body effects through the inclusion of \(\Sigma_1^{\infty}\), and they are sensitive to the choice of the correlation potential.

B. Divalent atoms

In Tables V, VI, and VII we present our results for the ionization potentials (removal of one \(s\) electron, IP1, and removal of both \(s\) electrons, IP1+IP2) and excitation energies for the lowest 31 levels for Ba, lowest 40 levels for Ra, and lowest 25 levels for E120. Results presented under the column “CP+SD+CI” mean that the all-orders correlation potential \(\Sigma_1^{\infty}\) is included (though ladder di-

| State | RHF + \(\Sigma_1^{\infty}\) | Lad. | Breit QED | Total Exp. \(\Delta\) |
|-------|----------------|------|----------|----------------|
| 6s1/2 | 75340          | -156 | -22      | -45 80585 -80680 -101 |
| 5d5/2 | 68139          | -763 | 34       | 36 75773 75812 -39 |
| 5d5/2 | 67665          | -765 | 57       | 32 74966 75011 -65 |
| 6p1/2 | 57266          | -128 | -36      | 5 60432 60425 7 |
| 6p1/2 | 55873          | -118 | -16      | 3 58734 58734 0 |
| 4f1/2 | 28213          | -32  | 117      | 32 32297 32428 -131 |
| 4f7/2 | 28222          | -32  | 126      | 28 32112 32203 -91 |

a NIST data, Ref. [42].
TABLE IV. Ionization energies for the lowest states in each wave to $l = 3$ for E120; units cm$^{-1}$.

| State   | RHF | $\Delta \Sigma^\infty$ | Ladder | Breit | QED | Total |
|---------|-----|-------------------------|--------|-------|-----|-------|
| $8^1s$  | 83168 | 90105                   | -520   | -108  | -129| 89349 |
| $8^1p$  | 60027 | 65475                   | -379   | -141  | -9  | 64946 |
| $7^3d$  | 56620 | 64841                   | -593   | 51    | 58  | 64357 |
| $7^5d$  | 56413 | 62684                   | -625   | 46    | 46  | 62151 |
| $8^1p$  | 49295 | 52017                   | -179   | -18   | -7  | 51812 |
| $6^3f$  | 29734 | 36907                   | -211   | 186   | 97  | 36978 |
| $6^5f$  | 29990 | 32652                   | -219   | 169   | 77  | 37279 |

Barium

For Ba, it is seen that the ladder diagrams give a contribution to the excitation energies of about 500 cm$^{-1}$ for configurations containing a single 5d orbital, that is for 6s5d and 5d6p (excluding the very highest level). For the 5d$^2$ configuration, the contribution amounts to roughly double this, $\approx 1000$ cm$^{-1}$. The ladder diagrams give a small correction to the other levels.

The Breit and radiative corrections for Ba are roughly of the same magnitude, ranging between about 10 – 120 cm$^{-1}$ for Breit and 15 – 110 cm$^{-1}$ for the radiative corrections for the levels considered. For the higher levels the radiative corrections dominate.

We see that the deviation of our final results “Total” from experiment, $\Delta_{\text{Exp}}$, ranges between 10 – 200 cm$^{-1}$, with the exception of the larger deviation for 5d$^2$3P_0,1 of about 400 cm$^{-1}$ and 500 cm$^{-1}$ and the very large deviation for 5d$^2$1S_0 of about 1100 cm$^{-1}$.

The singlet state 5d$^2$1G_4 has not been measured and is absent in the NIST data [42]. Its position was predicted in the early experimental work of Palenius [46] to be 24300±300 cm$^{-1}$. It has subsequently been calculated in the works [18, 47, 48]; there are other calculations of the barium spectra where this level has been missed. We present in the table, alongside our own result, the initial estimate [46] and the value from the most precise calculations [18]. Our calculations give the value 25205 cm$^{-1}$ for this level; looking at the results for other terms with the configuration 5d$^2$, we expect that the result for this level could be underestimated, possibly by as much as 100 – 300 cm$^{-1}$.

Our result for 5d$^2$1S_0 disagrees with the experimental value by $\approx 1100$ cm$^{-1}$. This very large difference is well outside the deviations we see for the other levels. This level does not appear in the extensive spectra calculations of Landau et al. [18]. We know of only one other calculation of this level, carried out in the CP+CI method with empirical fitting [20], with the result 26034 cm$^{-1}$; this is about 700 cm$^{-1}$ less than experiment, and well above the estimated error in that work.

We should note, however, that the largest deviations we see are for terms belonging to 5d$^2$, and the unmeasured level 5d$^2$1G_4 and the level 5d$^2$1S_0 belong to this configuration. It is possible that our calculations do not do an adequate job for these low-lying d$^2$ states. We note further the large difference between our result and that of Ref. [18] for the energy of the level 5d$^2$1G_4. The results of the current work are in significantly better agreement with experiment over the considered spectral range compared to the ab initio calculations performed using CP+CI [20], SD+CI [32], and a version of Fock-space coupled-cluster (FSCC) [42].

The QED correction to IP1 was calculated in the work [37] using the radiative potential [36], and the value $–19$ cm$^{-1}$ was obtained – the same result we have obtained in this work.

Radium

The results for radium are presented in Table VI. It is seen from the table that there are a number of gaps in the experimental data, and accurate theoretical predictions of the missing data are important. We don’t agree with all configuration designations used in the experimental data compiled by NIST [42], and we predict that the energy of one of the states (7s7p 1P_1) is significantly lower than that given in the data tables, as explained later.

Compared to Ba, the ladder contributions for Ra are smaller for the terms involving d orbitals in the dominant configurations, while the contributions to terms from the ss and sp configurations are larger. The Breit contributions to the excitation energies range from 10 – 81 cm$^{-1}$ for the levels considered, while we saw a significantly larger contribution arising from the QED radiative corrections, $37 – 180$ cm$^{-1}$.

Unlike the case with Ba, for Ra the term designations
change in some cases when we go from the approximation without ladder diagrams, CP\(^{\text{nl}}\) + SD + CI, to that with ladder diagrams. This means that it is more difficult to track the changes in energies associated with the ladder corrections, as the terms themselves may differ in these approximations.

The deviations from experiment are generally smaller for Ra than for Ba, with the deviations well under 100 cm\(^{-1}\) for most levels; only a few levels deviate more than 100 cm\(^{-1}\), with the maximum deviation 191 cm\(^{-1}\) for the singlet state 7\(s6d^1D_2\) (with the exception of 7\(s8p^1P_1\), which we address below).

In the final column of Table VI we list the results of other calculations. For the lower levels, we present the results of \textit{ab initio} calculations, namely from the CP + CI method \cite{29} and the extended intermediate Hamiltonian Fock-space coupled-cluster (XIHFS C) method \cite{31}. For the higher levels, where data from these methods is unavailable, we present the results of the IHFSCC method \cite{18} and a semi-empirical CP + CI calculation \cite{20}. Both of these calculations miss some of the higher levels that we see. Note that QED corrections to the excitation energies were not taken into account in these other works \cite{18, 29, 31}, while Breit corrections were also omitted in

| Conf. | Term | J   | CP\(^{\text{nl}}\) + SD + CI | Ladder | Breit | QED  | Total | Exp.\(^a\) | \(\Delta\)Exp | Other |
|-------|------|-----|----------------------------|--------|-------|------|-------|--------|------------|-------|
| IP1   | 6s\(^2\) | 1S  | 0  | 122905 | -329 | 100 | -64  | 122612 | 9117 | 9077 |
| IP1+IP2 | 6s\(^2\) | 1S  | 1  | 8460  | 575  | 70  | -60  | 8905  | 9034 | -129 |
| 6s5d  | 3D   | 0   | 2  | 8704  | 576  | 68  | -59  | 9153  | 9216 | -63  |
|       |      |     | 3  | 9066  | 576  | 61  | -57  | 9524  | 9597 | -73  |
| 6s5d  | 1D   | 0   | 1  | 12096 | 589  | -62 | -66  | 11457 | 11395 | 62   |
| 6s6p  | 3P\(^o\) | 0   | 1  | 12351 | -33  | 27  | -35  | 12310 | 12260 | 44   |
|       |      |     | 2  | 12706 | -33  | 26  | -35  | 12664 | 12637 | 27   |
| 6s6p  | 3P\(^o\) | 1   | 2  | 13603 | -41  | 25  | -32  | 13555 | 13515 | 40   |
|       |      |     | 3  | 17875 | 107  | 11  | -41  | 17964 | 18060 | -91  |
| 5d\(^2\) | 3F   | 2   | 2  | 19920 | 1142 | -119| -110 | 20833 | 20934 | -101 |
|       |      |     | 3  | 20142 | 1146 | -115| -108 | 21065 | 21250 | -185 |
| 5d6p  | 3F\(^o\) | 2   | 2  | 21545 | 545  | -46 | -96  | 21948 | 22065 | -117 |
|       |      |     | 3  | 22436 | 538  | -42 | -93  | 22839 | 22947 | -108 |
|       |      |     | 4  | 20636 | 1145 | -109| -106 | 21566 | 21624 | -58   |
| 5d\(^2\) | 1D   | 2   | 2  | 22182 | 996  | -86 | -103 | 22989 | 23062 | -73   |
| 5d6p  | 1D\(^o\) | 2   | 2  | 22607 | 543  | -48 | -94  | 23008 | 23074 | -66   |
|       |      |     | 1  | 22118 | 1020 | -90 | -104 | 22946 | 23480 | -534  |
|       |      |     | 2  | 22897 | 1003 | -81 | -100 | 23719 | 23919 | -534  |
| 5d6p  | 3D\(^o\) | 1   | 3  | 23635 | 541  | -61 | -98  | 24017 | 24192 | -175  |
|       |      |     | 2  | 23992 | 545  | -58 | -97  | 24382 | 24532 | -150  |
|       |      |     | 3  | 24460 | 543  | -56 | -95  | 24852 | 24980 | -128  |
| 5d\(^2\) | 1G   | 4   | 4  | 24328 | 1069 | -89 | -103 | 25205 | 24300 | 300   |
| 5d6p  | 3P\(^o\) | 0   | 1  | 25115 | 507  | -54 | -94  | 25474 | 25642 | -168  |
|       |      |     | 2  | 25183 | 503  | -51 | -92  | 25543 | 25704 | -161  |
| 6s7s  | 3S   | 1   | 2  | 26253 | -135 | 28  | -15  | 26131 | 26160 | -29   |
| 5d\(^2\) | 1S   | 0   | 2  | 25144 | 612  | -28 | -70  | 25658 | 26757 | -1099 |
| 5d6p  | 1F\(^o\) | 3   | 2  | 26343 | 498  | -56 | -94  | 26691 | 26816 | -125  |
| 6s7s  | 1S   | 0   | 2  | 28192 | 55   | 10  | -37  | 28220 | 28230 | -10   |

\(^a\) NIST data, Ref. \cite{42}.
\(^b\) IHFSCC, Ref. \cite{18}.
\(^c\) CP+CI, Ref. \cite{29}.
\(^d\) SD+CI, Ref. \cite{32}.
\(^e\) CP+CI, Ref. \cite{29}.
\(^f\) FSCC, Ref. \cite{45}.
\(^g\) Estimated in the experimental work of Palenius, Ref. \cite{46}.
\(^h\) Semi-empirical CP+CI, Ref. \cite{20}.
TABLE VI. Ionization potentials (removal of one electron, IP1, and both electrons, IP1+IP2) and excitation energies for Ra. CP$^{\text{a1}}$+SD+CI excludes ladder diagrams, Breit, and QED; these corrections are given in subsequent columns. $\Delta_{\text{Exp}} =$ Total − Exp. Results of other calculations are presented in the final column. Units: cm$^{-1}$. Asterisks (*) identify where configurations have been modified from those in the NIST data $^{42}$ or where calculated energies in the final column have been reassigned to different terms.

| Conf. | Term | J | CP$^{\text{a1}}$+SD+CI | Ladder | Breit | QED | Total | Exp$^{a}$ | $\Delta_{\text{Exp}}$ | Other |
|-------|------|---|--------------------------|--------|-------|-----|-------|---------|----------------|-------|
| IP1   | 7s$^2$ | 1$S$ | 0 | 42680 | -227 | 271 | -45 | 42679 | 42573 | 102 | 42622$^{b}$, 42562$^{c}$ |
| IP1+IP2 | 7s$^2$ | 1$S$ | 0 | 124690 | -446 | 250 | -132 | 124363 | 124416 | -53 | 124656$^{b}$, 124642$^{c}$ |
| 7s7p  | 3$^P^o$ | 0 | 13173 | -43 | 70 | -64 | 13136 | 13078 | 58 | 12916$^{b}$, 13093$^{c}$ |
|       |        | 1 | 14080 | -47 | 71 | -64 | 14040 | 13999 | 41 | 13544$^{b}$, 14017$^{c}$ |
|       |        | 2 | 16828 | -84 | 78 | -60 | 16762 | 16689 | 73 | 16566$^{b}$, 16675$^{c}$ |
| 7s6d  | 3$D$   | 1 | 13411 | 380 | -46 | -92 | 13653 | 13716 | -63 | 13622$^{b}$, 14021$^{c}$ |
|       |        | 2 | 13771 | 384 | -39 | -91 | 14025 | 13994 | 31 | 13902$^{b}$, 14292$^{c}$ |
|       |        | 3 | 14440 | 401 | -20 | -85 | 14736 | 14707 | 29 | 14645$^{b}$, 14898$^{c}$ |
| 7s6d  | 1$D$   | 2 | 16996 | 385 | -12 | -97 | 17272 | 17081 | 191 | 17004$^{b}$, 17376$^{c}$ |
| 7s7p  | 1$F^o$ | 1 | 20632 | -34 | 69 | -61 | 20606 | 20716 | -110 | 20667$^{b}$, 20792$^{c}$ |
| 7s8s  | 3$S$   | 1 | 26887 | -181 | 73 | -37 | 26742 | 26754 | -12 | 26665$^{b}$, 26762$^{c}$ |
| 7s8s  | 1$S$   | 0 | 27910 | -119 | 70 | -45 | 27816 | 27915 | 99 | 27768$^{b}$, 28248$^{c}$ |
| 6d7p  | 3$F^o$ | 2 | 27803 | 337 | 26 | -161 | 28005 | 28038 | -33 | 27991$^{b}$, 28328$^{c}$ |
|       |        | 3 | 29924 | 328 | 46 | -155 | 30143 | 30118 | 25 | 30067$^{b}$, 30388$^{c}$ |
|       |        | 4 | 32248 | 303 | 59 | -151 | 32549 | 32368 | 91 | 32363$^{b}$, 32603$^{c}$ |
| 6d$^2$ | 3$F$   | 2 | 28964 | 738 | -67 | -180 | 29455 | 29731$^{b}$, 29610$^{c}$ |
|       |        | 3 | 29648 | 776 | -56 | -179 | 30189 | 30464$^{b}$, 30404$^{c}$ |
|       |        | 4 | 30455 | 787 | -39 | -175 | 31028 | 31172$^{b}$, 31114$^{c}$ |
| 6d$^2*$ | 3$P$  | 0 | 29426 | 402 | 32 | -155 | 29705 | 29840$^{b}$, 29833$^{c}$ |
|       |        | 1 | 30595 | 560 | 10 | -164 | 31065 | 31249 | -184 | 31365$^{b}$, 31342$^{c}$ |
|       |        | 2 | 31892 | 1257 | 22 | -142 | 33029 | 32941 | 88 | 33180$^{b}$, 33147$^{c}$ |
| 7s8p  | 1$P^o$ | 1 | 30691 | 51 | 55 | -94 | 30703 | 32858 | -2155 | 30695$^{b}$ |
| 6d$^2$ | 1$D$   | 2 | 30490 | 493 | 13 | -144 | 30852 | 30982$^{b}$, 30938$^{c}$ |
| 6d7p  | 1$D^o$ | 2 | 30747 | 312 | 43 | -150 | 30952 | 30918 | 34 | 30894$^{b}$, 31178$^{c}$ |
| 7s8p  | 3$P^o$ | 0 | 31180 | -152 | 79 | -53 | 31054 | 31086 | -32 | 31008$^{b}$, 31126$^{c}$ |
|       |        | 1 | 31511 | -5 | 55 | -88 | 31473 | 31563 | -90 | 31446$^{b}$, 31636$^{c}$ |
|       |        | 2 | 31913 | -92 | 75 | -64 | 31832 | 31874 | -42 | 31778$^{b}$, 31934$^{c}$ |
| 7s7d  | 3$D$   | 1 | 32079 | -144 | 74 | -51 | 31958 | 32001 | -43 | 31895$^{b}$, 32423$^{c}$ |
|       |        | 2 | 32749 | -810 | 69 | -65 | 31943 | 31993 | -50 | 31902$^{b}$ |
|       |        | 3 | 32273 | -143 | 77 | -51 | 32156 | 32197 | -41 | 32068$^{b}$, 32625$^{c}$ |
| 7s7d$^a$ | 1$D$ | 2 | 32171 | 26 | 53 | -84 | 32166 | 32215 | -49 | 32205$^{b}$, 32564$^{c}$ |
| 6d7p  | 3$D^o$ | 0 | 33021 | 254 | 28 | -147 | 33156 | 33197 | -41 | 33169$^{b}$, 33531$^{c}$ |
|       |        | 2 | 32287 | 279 | 17 | -157 | 32426 | 32507 | -81 | 32436$^{b}$, 32946$^{c}$ |
|       |        | 3 | 33000 | 254 | 28 | -147 | 33156 | 33197 | -41 | 33169$^{b}$, 33531$^{c}$ |
| 6d$^2$ | 1$G$   | 4 | 33142 | 724 | -16 | -166 | 33684 | 33261$^{b}$ |
| 6d$^2$ | 1$S$   | 0 | 33561 | 312 | 54 | -116 | 33811 | 33961$^{b}$ |
| 6d7p  | 1$F^o$ | 3 | 34230 | 155 | 55 | -121 | 34319 | 34332$^{b}$ |
| 7s9s  | 3$S$   | 1 | 34601 | -224 | 81 | -41 | 34417 | 34476 | -59 |
Ref. [29]. In Ref. [31], the value for IP1 was modified by adding the frequency-dependent Breit and radiative QED corrections from Ref. [32]; the contribution from the radiative corrections, through use of the radiative potential [36], is $-42$ cm$^{-1}$, in agreement with the current work. In Ref. [29], while Breit and QED radiative corrections were not included explicitly, these effects were taken into account to some degree through the empirical fitting factors.

The current calculations for radium are the most complete and most accurate to date. With the high accuracy that we have achieved using this method, we can be confident of resolving anomalies with experiment in favour of the theoretical predictions.

The most striking disagreement is with the energy assigned to the state $7s8p \, ^3P_0^o$. In the experimental data [12], the large excitation energy 32858 cm$^{-1}$ is given to this state. However, we do not see this level in our calculations; rather, we see a low-lying state, with energy 30703 cm$^{-1}$, that is absent in the data. In the relativistic regime, the states are defined by their total angular momentum $J$ and their parity. We see only six levels with $J = 1$ and odd parity in the energy range we have considered, and even extending this range, the next level that we see appears as high as 30667 cm$^{-1}$.

As for other supporting theoretical calculations for the $^1P_1^o$ anomaly, results of the semi-empirical CP+CI calculation [30] included two levels with $J = 1$ and odd parity with energies 30695 cm$^{-1}$ and 31446 cm$^{-1}$. These were assigned in that work to the two levels $7s8p \, ^3P_1$ and $7s8p \, ^1P_0$ in the experimental data, with very large deviations $-868$ cm$^{-1}$ and $-1412$ cm$^{-1}$ being seen there. We suggest that these calculated excitation energies should instead be assigned to the low-lying levels $7s8p \, ^3P_1$ and $7s8p \, ^3P_0$. These numbers are in very close agreement with the results of the current work, 30703 cm$^{-1}$ and 31473 cm$^{-1}$. No data for the corresponding singlet state $^1P_0^o$ was presented in the IHFSCC work [18].

Therefore, we suggest that there is no high-lying singlet state $^1P_0^o$ with energy 32858 cm$^{-1}$, though we expect that there should be a lower-lying one with energy around 30700 cm$^{-1}$.

We also suggest that configuration assignments for some terms be altered. We do not have any terms in our data with leading configuration $7p^2$ as appears in the experimental data. For the triplet terms $7p^2 \, ^3P$, our results indicate instead a strongly dominating configuration $6d^2 \, ^3P$. There is also a case where we see that the dominant configuration is $7s7d$ rather than $7p^2$, for the term referred in the experimental data as $7p^2 \, ^1D_2$.

In a system as heavy as radium, and particularly for the higher levels, the validity of the LS system for designating the terms loses much of its meaning. Nevertheless, we still believe that making the previous observations is important, especially when different assignment of the configurations may lead to confusion between the designations of levels.

We note further, that with the very strong mixing of configurations in some terms, these designations become less clear, as we have seen for the odd-parity $J = 1$ terms $7s8p \, ^1P_1$, $7s8p \, ^3P_0$, and $6d7p \, ^3P_1$, where the mixing between $7s8p$ and $6d7p$ is very strong.

3. Element 120

Our results for the ionization potentials and excitation energies for E120 are presented in Table VII. We also present the results of our calculations for $q$-factors, and the corresponding non-relativistic values, to help in identification of the levels. For the higher levels, there is strong mixing between configurations, and we have included the dominant configurations explicitly in the table.

It is seen that the ladder diagrams for E120 are significant, around 400 cm$^{-1}$ for many levels, although the maximum correction for the levels for E120 is less than we saw for the lighter atoms. The $d$ orbitals are well-screened by the relativistically contracted $s$ and $p_{1/2}$ orbitals, and there are no low-lying terms with $d^2$ configuration.

The Breit corrections to the excitation energies are about 150 cm$^{-1}$ for many levels, while the QED radiative corrections are smaller, reaching 158 cm$^{-1}$ in the largest case, for the level $8p^2 \, ^1S_0$.

In the final columns we list the results of other ab initio calculations. CP+CI [20], a version of FSCC [30], and XHFCSCC [31]. We are also aware of another calculation [38] of the excitation spectra of E120, though the results are so different from all other data (by as much as 10000 cm$^{-1}$ for some levels) that we have decided not to present them in the table.

Overall, there is good agreement between the different calculations presented in the table. It should be noted that Breit and QED corrections were not included in the calculations [29], while QED was not included in Refs. [30, 31]. Also, there is some sensitivity to the choice of nuclear density. We used the same Fermi distribution that was used in the previous calculation [29], and in that work the volume isotopic shifts were studied; we refer the reader to that work for more details.

The QED radiative correction to the ionization potential IP1 for E120 was calculated recently. Shabaev et al. used their model operator approach [50] to calculate the self-energy correction; they obtained $-202$ cm$^{-1}$. The total QED correction (including vacuum polarization) was calculated in Ref. [37] using the radiative potential method [36], and they obtained a result of $-77$ cm$^{-1}$, in excellent agreement with our own $-75$ cm$^{-1}$. Their result is broken down into the self-energy and vacuum polarization contributions, $-183$ cm$^{-1}$ and $+106$ cm$^{-1}$, with the former in good agreement with the result of Shabaev et al.

The only other calculation of QED corrections to excitation energies for E120 was performed in the work [38]. The corrections were found using the radiative potential
method \cite{36} implemented in GRASP \cite{37,39,40}, with results in very good agreement with the results of this work.

4. Accuracy

The quality of our calculations can be gauged by comparison of our results with experiment. We found excellent agreement between theory and experiment for barium and radium, \( \lesssim 100 \text{ cm}^{-1} \) for many cases, and we can expect a similar level in the error for our predictions for \( \text{E}120 \).

We note that the largest deviations we have seen between theory and experiment mostly involve configurations containing \( d \)-orbitals. The smaller deviations we see for Ra compared to Ba could be due to the \( d \)-orbitals being screened (also there are fewer configurations involving \( d \)-orbitals in the lower levels); this screening effect is even more pronounced for \( \text{E}120 \), and therefore the associated errors from \( d \)-orbitals may be reduced.

To further study the limits of our method, particularly in relation to the quality of the correlation potential, we have also performed calculations of the spectra for the three atoms using a different set of screening factors for the Coulomb interaction in the exchange part of the correlation potential. The screening factors were found from the direct diagrams with both electron-electron screening and the hole-particle interaction included, see the second row of Table I. Calculations performed with these modified screening factors gave results that differed from our final results “Total” in Tables VI, VII, VIII over the full spectral range we considered by about 10 – 200 cm\(^{-1}\) for barium, about 10 – 100 cm\(^{-1}\) for radium, and about 10 – 200 cm\(^{-1}\) for element 120. For E120, the largest deviations occurred for the higher levels corresponding to configurations comprised of valence orbitals that are not the lowest for that wave. For many of the levels for Ba and Ra, the results with the adjusted screening factors were better than or as good as the original results (and often on the other side of the experimental values). Therefore, we estimate an error that is about half the size.
of these shifts, consistent with the error estimates we obtained by looking at the deviation of the original results from experiment. We expect similar behaviour for E120.

IV. CONCLUSION

In summary, we have performed ab initio calculations of the spectra of Ba, Ra, and E120 using the recently-developed CP+SD+CI method. We have found unprecedented agreement with experiment for Ba and Ra and have made accurate predictions for missing and unreliable data and for the spectra of E120. For Ra, we are confident that the energy assigned to the level $7s8p^1P^0_1$ in the data \[42\] is incorrect, and we predict a value $\approx 2200\,\text{cm}^{-1}$ smaller. The size of the error for our calculations for Ra is about $100\,\text{cm}^{-1}$ or better, while it is slightly larger for Ba. We estimate a similar level of uncertainty for the spectra of E120. Finally, we note that the size of the errors in this ab initio method is comparable to the size of the QED radiative corrections.

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