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Theoretical determination of the ionization potentials of CaF, SrF, and BaF

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We present a comprehensive theoretical study of the ionization potentials of the MF (M = Ca, Sr, and Ba)
molecules using the state-of-the-art relativistic coupled-cluster approach with single, double, and perturbative
triple excitations [CCSD(T)]. We have further corrected our results for higher-order excitations (up to full triples)
and the QED self-energy and vacuum-polarization contributions. We have performed an extensive investigation
of the effect of the various computational parameters on the calculated ionization potentials, which allowed us
to assign realistic uncertainties to our predictions. For CaF and BaF, where precise experimental measurements
are available, our predictions are in excellent agreement with the measured values. In the case of SrF, we provide
a theoretical prediction of the ionization potential that deviates from the available experimental measurements,
motivating further experimental investigations.

I. INTRODUCTION

Ionization potentials (IPs) play a crucial role in understanding the behavior of atoms and molecules, thereby serving as a fundamental concept in both chemistry and physics. They provide valuable information about the electronic structure of atoms and molecules, enabling the determination of energy levels and the electronic configurations. Knowledge of the accurate values of ionization potentials contributes to the development and refinement of theoretical models and computational methods and facilitates understanding of quantum phenomena, such as electron correlation, many-body interactions, and the behavior of excited states. The ionization potentials of all the naturally occurring elements have been determined experimentally, mostly to very high precision [1]. Considerable progress in measuring the IPs of the heavier actinides has been made in recent years; No ($Z = 102$) [2] and Lr ($Z = 103$) [3] are the heaviest elements in which the IPs have been measured using challenging one-atom-at-a-time experimental techniques. Accurate measurements of molecular ionization potentials are much more scarce, even for the simplest molecules, composed of only two atoms. However, such measurements that provide accurate fundamental information about the molecules hold immense importance in the context of precision experiments on atoms and molecules.

Table-top molecular experiments offer a distinct avenue to explore physics beyond the standard model and the potential violation of fundamental symmetries, such as time reversal ($\mathcal{T}$) and parity ($\mathcal{P}$) symmetries [4,5]. Molecular electronic structure leads to enhancements of the tiny effects of the various $\mathcal{P}$- and $\mathcal{P}, \mathcal{T}$-violating phenomena, bringing these into the reach of experimental precision [4,6]. Compared with atoms and polyatomic molecules, diatomic molecules have additional significant advantages, one of which is that calculations on diatomic molecules are not very computationally expensive, allowing highly accurate theoretical investigations. Furthermore, certain diatomic molecules can be laser-cooled to ultracold temperatures [7,8], increasing the interaction times and offering opportunities to explore phenomena such as quantum degeneracy, ultracold chemistry, and quantum simulation [9–11], which have implications for both fundamental physics and quantum information science. These challenging experiments greatly benefit from reliable theoretical support, from the planning stage to the analysis of the results. In particular, interpretation of experiments searching for violation of fundamental symmetries requires knowledge of various coupling parameters, which are needed to extract the properties of interest [e.g., the magnitude of the electric dipole moment of the electron (eEDM) or the anapole moment of a certain nucleus] from the measured energy shifts [4,12]. These parameters depend on the molecular electronic structure and cannot be measured, and hence have to be provided through theoretical investigations.

Clearly, such theoretical predictions should be based on accurate and reliable calculations, performed using state-of-the-art computational methods that treat both electron correlation and relativistic effects on a high level. It is also of great importance in an experimental context to provide uncertainty estimates along with any predicted values. Performance

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of the employed computational tools and the schemes for error estimation should thus be benchmarked against known accurate experimental values to explore their reliability and predictive power for systems and properties where no experiment is available.

The relativistic coupled-cluster approach is considered to be one of the most powerful tools for the treatment of heavy many-electron systems. It has demonstrated a high accuracy and strong predictive power for a variety of atoms and molecules across different properties [13,14]. Recently, we have developed a scheme that allows us to determine uncertainties on the calculated properties by performing an extensive study of the effect of the different computational parameters on the results [15,16].

In this work, we apply the relativistic coupled-cluster approach to the alkaline-earth-metal monofluoride molecules, MF, where M = Ca, Sr and Ba. Group II fluorides benefit from a relatively simple electronic structure that allows for their laser cooling [17–19] and facilitates the interpretation of the experimental results. BaF is considered for precision measurements aimed to set a new upper limit on the electric dipole moment of the electron [20] and to measure the anapole moment of the ^{137}Ba nucleus [21]. Such experiments require input from theory for their interpretation [12,22], and benchmarking the calculations of these systems for properties where experiment is available is crucial. We thus apply our method of choice to theoretical predictions of ionization potentials of the MF molecules and include uncertainty estimates.

Numerous theoretical studies of the electronic structure and other properties of CaF, SrF, and BaF have been carried out using a variety of methods [16,18,23–26]. Experimental investigations have mainly been dedicated to measuring various spectroscopic properties of these molecules [1,27–36], such as molecular dipole moments and suitability for laser cooling [17,18]. The ionization potentials of CaF and BaF were measured in the 1990s using Rydberg spectroscopy [37,38], and a much earlier value is available for SrF [39] obtained from an electron-impact measurement. The aim of this work is thus twofold: to benchmark the quality of our calculations against accurate experimental values in the cases of CaF and BaF and to provide an accurate and reliable prediction for SrF, where there are a few low-precision experimental measurements available [39–42]. In the following, Sec. II presents the methods and computational details employed in this work. Section III contains the calculated values, while in Sec. IV the procedure for uncertainty evaluation used in this work is outlined. The final recommended values, along with comparison to earlier calculations and experiments, are presented in Sec. V.

II. METHOD AND COMPUTATIONAL DETAILS

All the calculations in this work were carried out using the developer's version of the DIRAC code [43,44], which allows us to use relativistic methods, in particular, the traditional four-component Dirac-Coulomb (DC) Hamiltonian.

The single-reference coupled-cluster approach with single, double (CCSD), and perturbative triple excitations [CCSD(T)] was used in all the calculations.

In order to take full advantage of this state-of-the-art approach, we used the relativistic Dyall basis sets [45,46]. These basis sets are available in different qualities, vnz (n = 2, 3, and 4). Furthermore, one can employ the "valence" (dyall.vnz), the "core-valence" (dyall.cv$n$z), or the "all-electron" (dyall.ae$n$z) variants of the basis sets of the same principal number; the latter two include extra core-valence-correlating and core-correlating functions, respectively. Finally, extra layers of diffuse functions can be added, designated by k-aug-vnz, with k = s (single), d (double), etc. The presence of diffuse functions improves the description of the bond region and hence of the valence properties.

The following procedure was employed for the calculations of the molecular ionization potentials. We calculated the potential energy curves of both the neutral molecule and the molecular ion of MF (M = Ca, Sr, and Ba) using the DC-CCSD(T) approach and different basis sets. The ionization potential was extracted as the difference between the energies of MF and MF$^+$ at the corresponding equilibrium bond lengths. The final results were obtained from a complete basis-set limit (CBSL) extrapolation of the potential energy curves based on the the s-aug-c$n$vz (n = 2, 3, and 4) basis sets and carried out following the scheme of Helgaker *et al.* [47] (H-CBSL). While this scheme is one of the most popular CBSL extrapolation approaches, we also test two other possibilities: the scheme of Martin [48] and the scheme of Lesiuk and Jeziorski [49]. These results are consistent to within 1 meV (with the H-CBSL value in between the two other values), confirming the convergence of the calculated IP with the respect to the basis-set cardinality. Using these results, the adiabatic IPs and spectroscopic molecular properties were extracted.

III. RESULTS

Table I contains the calculated spectroscopic constants of the ground states of the neutral molecules and molecular ions, compared to earlier theoretical predictions and experimental values, where available. In these calculations, we used the DC-CCSD(T) approach combined with the complete basis-set (CBS) extrapolation of the basis sets. For CaF, SrF, and BaF, the active correlation space included 25, 35, and 35 electrons, respectively, and the virtual space cutoff was set at 50 a.u. Our results are in a good agreement with previous calculations and experimental values. The least numerically stable value is the anharmonicity correction $\omega_e \chi_e$. However, for these constants the experimental uncertainty is often rather high.

In Table II, the IP values obtained using different basis sets are presented. These calculations were carried out correlating 25, 35, and 35 electrons, respectively, and setting the virtual space cutoff at 50 a.u.

For CaF, the difference between s-aug and d-aug is a bit larger than the corresponding difference between dyall.cv4z and s-aug, while this is not the case for SrF and BaF where the presented trend looks reasonable. We found that in the case of CaF, the d-aug basis set suffered from linear dependencies. To alleviate this issue, we removed the two outermost diffuse f-symmetry functions of the F atom.

TABLE I. Spectroscopic constants of the ground states of MF (M = Ca, Sr, and Ba) and their corresponding ions, calculated on the DC-CCSD(T) level. Results are based on the CBS extrapolation limit and 25, 35, and 35 electrons were correlated, respectively, with the virtual space cutoff at 50 a.u. ω_e and $\omega_e \chi_e$ are shown in cm^{-1}.

R_e (Å)	ω_e	$\omega_e \chi_e$	Ref.	Method
		CaF		
1.953	588.1	3.03	TW[a]	CCSD(T)
1.958	586.2	2.90	[23]	FSCC[b]
2.001	572.4	2.70	[50]	MRCI[c]
1.971	612.5	3.70	[51]	MRCI
1.967	—	—	[1]	Expt.
—	581.1(9)	—	[29]	Expt.
		CaF$^+$		
1.871	693.5	2.78	TW	CCSD(T)
		SrF		
2.076	501.1	1.9	TW	CCSD(T)
2.083	500.1	2.45	[23]	FSCC
2.137	475.0	—	[52]	MRCI
2.076	—	—	[27]	Expt.
—	502.4(7)	2.27(21)	[30]	Expt.
—	501.9650(1)	2.20462(4)	[34]	Expt.
		SrF$^+$		
1.996	587.9	2.16	TW	CCSD(T)
		BaF		
2.162	467.6	2.32	TW	CCSD(T)
2.177	468.4	1.83	[23]	FSCC
2.171	474.1	1.90	[24]	MRCI+SOC
2.159296(8)	—	—	[53]	Expt.
—	469.4	—	[54]	Expt.
—	—	1.8373(8)	[55]	Expt.
		BaF$^+$		
2.087	538.3	1.92	TW	CCSD(T)

[a]This work.

[b]Fock-space coupled-cluster approach.

[c]MultiReference Configuration Interaction method.

The adiabatic IPs, derived from the molecular energies calculated at the equilibrium bond lengths of the neutral molecules and the molecular ions, were further corrected for higher-order correlations and relativistic contributions.

TABLE II. Adiabatic IPs (eV) of MF (M = Ca, Sr, and Ba) obtained using basis sets of differing quality. The results were obtained within the CCSD(T) approach, correlating 25, 35, and 35 electrons, respectively, and including virtual orbitals up to 50 a.u.

Basis set	CaF	SrF	BaF
dyall.v3z	5.8897	5.3949	4.8072
dyall.cv3z	5.8257	5.4014	4.8043
dyall.ae3z	5.8257	5.4014	4.7967
dyall.cv4z	5.8199	5.4075	4.7991
s-aug-dyall.cv4z	5.8280	5.4152	4.8026
d-aug-dyall.cv4z	5.8266[a]	5.4155	4.8030
s-aug-dyall.cv$n$z H-CBSL	5.8236	5.4174	4.8035

[a]Modified basis sets, 2-f functions were removed.

TABLE III. Adiabatic IPs (eV) of MF (M = Ca, Sr, and Ba). Limited active space is orbitals with energies above −20 a.u. and a virtual space cutoff of 50 a.u.

Basis set	Active space	CaF	SrF	BaF
dyall.cv4z	Limited active space	5.8199	5.4075	4.7991
dyall.cv4z	Full active space	5.8206	5.4068	4.8006
dyall.ae4z	Full active space	5.8206	5.4068	4.7979

To correct for the limited active space used, we calculated the difference between the results obtained correlating electrons occupying orbitals with energies above −20 a.u. and a virtual space cutoff of 50 a.u. and those obtained correlating all electrons (29, 47, and 65, for CaF, SrF, and BaF, respectively) with a corresponding virtual space cutoff of 2000 a.u. In order to capture the full active space effect and to account for innercore correlations, the all-electron quality basis sets were used in the latter calculations. For these calculations, we used the dyall-cv4z and dyall-ae4z basis sets. The results are shown in Table III.

We evaluated the effect of the residual triple excitations [beyond (T)] by comparing the IPs calculated at the CCSDT and CCSD(T) levels of theory using the MRCC code [56]. These calculations were performed using the dyall.v3z basis sets, correlating 15, 17, and 17 electrons for MF, M = Ca, Sr, and Ba, respectively, and with a virtual space cutoff set at 10 a.u. As the effect was very small (about 1 meV), we did not consider excitations beyond triples.

QED corrections were calculated using the development version of the DIRAC program package [44]. The Uehling potential [57] was employed for the vacuum polarization and the effective potential of Flambaum and Ginges was employed for the electron self-energy [58]. We added the effective QED potentials to the Ca, Sr, and Ba nuclei.

The electronic structure of the MF molecules is very similar to that of M^+, and the valence electron is removed from a nonbonding atomiclike orbital. Thus, we calculated the effect of the Breit contribution on the IP of M^+. The Breit calculations were performed within the Fock-space coupled-cluster approach (FSCC), using the TEL AVIV atomic computational package [59].

Finally, we corrected our results for the effect of missing augmentation functions by taking the difference between the s-aug-dyall.cv4z and the d-aug-dyall.cv4z values (Table II).

All the corrections were calculated at the equilibrium geometries of neutrals and ions of MF molecules and added to our baseline IPs from Table II, obtained at the CBS limit. The individual contributions can be seen in Table IV.

IV. UNCERTAINTY ESTIMATES

Reliable estimates of the uncertainty of theoretical predictions of molecular properties is crucial for the support and interpretation of experiments that aim to investigate the systems in question. These uncertainty estimates can be obtained from extensive computational investigations; we have successfully employed such procedures in the past for various atomic and molecular properties [15,16,22,60].

TABLE IV. Calculated IPs of MF (M = Ca, Sr, and Ba) (eV) including higher-order contributions.

Method	CaF	SrF	BaF
DC-CCSD	5.8180	5.3940	4.7700
DC-CCSD(T)	5.8236	5.4174	4.8036
+augmentation	−0.0015	0.0003	0.0004
+core corr.+active space	0.0007	−0.0007	−0.0012
+ΔT	0.0005	0.0008	0.0010
+Breit	−0.0010	−0.0011	−0.0009
+QED	−0.0008	−0.0020	−0.0031
Final result	5.8216	5.4148	4.7998

The three main sources of uncertainty in our calculations are the incompleteness of the employed basis set, approximations in the treatment of the electron correlation, and the missing relativistic effects. As we are considering higher-order effects, we assume these sources of error to be largely independent, so we can treat them separately. In the following, each of these contributions is presented and evaluated separately; the individual contributions to the total uncertainty are given in Table V.

a. Basis set. To evaluate the basis-set incompleteness error, we consider the basis-set cardinality and the convergence in terms of core-correlating functions and diffuse functions. The final results were obtained at the CBS level. We evaluate the cardinality incompleteness error as half of the difference between CBS and s-aug-dyall.cv4z basis-set results. The effect of using a limited number of core-correlating functions is considered in the next section. The remaining uncertainty due to the possible lack of additional diffuse functions is evaluated as the difference between the results obtained using the doubly augmented and the singly augmented dyall.cv4z basis sets.

b. Electron correlation. We consider separately the effect of using a limited active space (virtual space cutoff) and the effect of excitations beyond perturbative triples. To account for the virtual space cutoff, we take the difference between results obtained with a virtual cutoff of 50 and 2000 a.u. at the dyall.cv4z basis-set level correlating 25, 35, and 35 electrons for MF, where M = Ca, Sr, and Ba, respectively. In order to capture the effect of innercore correlating functions, we estimate the difference between the calculation with the all-electron quality basis set (dyall.ae4z) and the standard dyall-cv4z basis set, while correlating all electrons in active space for both calculations. We take the contribution of the

TABLE V. Main sources of uncertainty in the calculated IP of MF (M = Ca, Sr, and Ba) (meV).

Category	Error source	CaF	SrF	BaF
Basis set	Cardinality	2.21	1.10	0.50
	Augmentation	1.47	0.27	0.37
	Innercore functions	0.01	0.00	2.72
Correlation	Virtual space	1.23	0.15	0.44
	Higher excitations	0.53	0.84	0.97
Relativity	QED	0.12	0.54	1.28
Total uncertainty (meV)		2.98	1.52	3.25

TABLE VI. Recommended theoretical IP of MF (M = Ca, Sr, and Ba) (eV) with uncertainties.

IP	CaF	SrF	BaF
Vertical	5.891	5.476	4.849
Adiabatic	5.821(3)	5.415(1)	4.800(3)
Adiabatic + ZPE[a]	5.828(3)	5.420(1)	4.804(3)
Experiment[b]	5.8270(6)	5.36–5.62	4.80377(1)

[a]Zero point vibrational energy (ZPVE).
[b]CaF [65], SrF [66], and BaF [38].

residual triple excitations (ΔT) as the estimate of the error due to neglecting higher-order excitations. Note that the uncertainty estimation is a bit conservative, because including higher-order corrections often exhibit different signs, potentially canceling out to a significant extent.

c. Relativistic effects. The Uehling and Flambaum-Ginges potentials can include the lowest QED contribution with $Z\alpha^2$, where α is the fine-structure constant. The next order should be $Z^2\alpha^3$ in atomic units from the expansion of the bound-state propagator for the self-energy effect [44]. From this, we may estimate the contribution from the next order by substituting the nuclear charge Z for Ca, Sr, and Ba, and taking the ratio.

The magnitudes of the various effects contributing to the uncertainty are given in Table V and the total uncertainty is obtained by combining all the above terms and assuming them to be independent.

V. FINAL VALUES

The final recommended adiabatic IPs of MF (M = Ca, Sr, and Ba), along with the corresponding uncertainties, are presented in Table VI. To make an accessible comparison with experiment we also present the vibrationally corrected adiabatic IP$_{vc}$, defined in the following way:

$$\text{IP}_{vc} = \left(E^{MF^+} + \tfrac{1}{2}\omega_e^{MF^+} - \tfrac{1}{4}\omega_e\chi_e^{MF^+} \right) - \left(E^{MF} + \tfrac{1}{2}\omega_e^{MF} - \tfrac{1}{4}\omega_e\chi_e^{MF} \right), \quad (1)$$

where E^{MF^+} and E^{MF} are the energies of the ion and the neutral systems (M = Ca, Sr, and Ba) at the corresponding equilibrium bond lengths, $\omega_e^{MF^+}$ is the vibrational frequency of MF$^+$, and ω_e^{MF} is the vibrational frequency of MF (Table I).

Measurements of the IPs of CaF, SrF, and BaF have utilized different experimental techniques and are presented in Fig. 1 alongside our calculations. Electron-impact (EI) measurements, shown as red triangles, have been performed for CaF [61,62], SrF [39,42], and BaF [39,42,63,64] and are taken from the NIST Webbook. The IPs of CaF [65] and BaF [38] have also been determined through extrapolation of observed Rydberg series to the ionization limit and are shown as light blue squares in the main plots and light blue horizontal bands in the insets. A resonance-enhanced multiphoton ionization (REMPI) study of SrF obtained a limit for where its IP must lie within, according to the total photon energies of a two-step scheme and a three-step scheme [66]. This range is shown as an orange band in Fig. 1. For CaF and BaF, insets are displayed in Fig. 1 showing the deviation in meV between our calculations and the Rydberg series IP measurements.
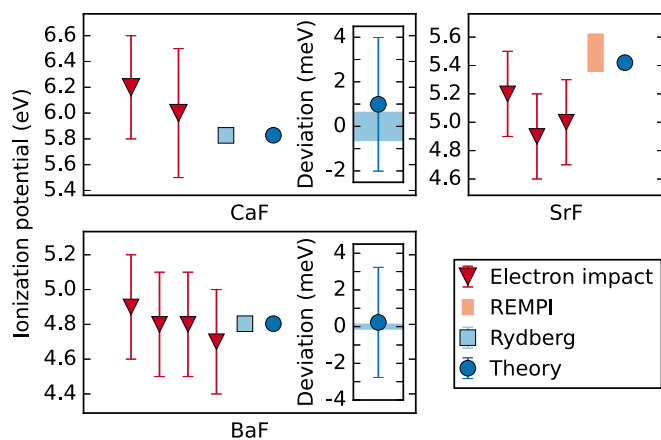
FIG. 1. Ionization potential measurements (in eV) of CaF, SrF, and BaF compared with calculations from this work. Electron-impact measurements [39,42,61–64] are shown as red triangles. IPs determined through Rydberg series measurements [38,65] and calculated IPs are shown as light blue squares and dark blue circles, respectively. The uncertainties on these measurements and calculations are smaller than the markers in the main plots. REMPI studies of SrF [66] showed its IP must lie between the range denoted by the orange band. For CaF and BaF, the displayed insets show the deviation in meV between the Rydberg series determinations (light blue vertical bands) and calculated IPs (dark blue circles).

The IPs obtained from the available EI measurements are of a limited precision and have uncertainties in the hundreds of meV range. This limited precision is, in part, due to difficulties in producing tunable, monochromatic electron beams. Furthermore, EI measurements can also suffer from systematic uncertainties stemming from their nonselectivity as an ionization method. Ions can be created from thermally populated states other than the ground state, leading to a lower observed ionization threshold. In addition, dissociation of larger products that result in ionic fragments with the same mass-to-charge ratio under investigation can lead to erroneous IP measurements.

In contrast, extrapolating to the convergence limit of the observed series of Rydberg states allows for accurate, high-precision determinations of IPs, in part, due to the excellent degree of quantum-state selectivity that multiply resonant excitation schemes enable. These Rydberg series measurements act as stringent and reliable tests of theory. As can be seen from the insets of Fig. 1, our calculations are in excellent

agreement with the Rydberg series IP measurements of CaF and BaF, deviating from the precise experimental results by around 1 meV or less.

The high degree of agreement between our calculations and the precise experimental values available for CaF and BaF showcases the accuracy of our computational approach and the reliability of the scheme that we have used to assign uncertainties to our predictions. In the case of SrF, we obtain a larger value than the EI measurements. Our value is, however, consistent with the limit set on the SrF IP determined from REMPI studies. Given the simultaneous accuracy and precision of our calculations, as proven by the excellent agreement with the reliable Rydberg series IP measurements of CaF and BaF, researchers could use our IP calculation for planning ionization-detected experiments of SrF. The lack of a precise and reliable value of the SrF IP could motivate its accurate measurement, in addition to the heavier monofluoride homolog RaF [67,68].

VI. CONCLUSIONS

We performed calculations of the IPs of CaF, SrF, and BaF, using the four-component [CCSD(T)] method and employing large uncontracted basis sets with extrapolation to the CBS limit. Breit, QED, and higher-order excitation corrections were added *a posteriori* to the CCSD(T) values. An extensive analysis of the effect of the various computational parameters allowed us to assign realistic uncertainties to our predictions. The calculated IPs of CaF and BaF are in excellent agreement with the experimental values, while for SrF, we provide a theoretical prediction of the IP.

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