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Ab initio calculations of the static dipole polarizabilities of CaF, SrF and BaF

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Abstract

In this work, ab initio computational methods are used to determine the static dipole polarizabilities of the $X^2\Sigma^+$ ground levels of the alkaline earth monohalides (CaF, SrF and BaF) with the finite-field approach in the zero-field limit. Results are obtained with the relativistic Hartree-Fock and coupled-cluster methods. The CCSD(T) values of the polarizabilities of CaF are $\alpha_{\parallel} = 99.421$ a.u. and $\alpha_{\perp} = 145.982$ a.u., for SrF they are $\alpha_{\parallel} = 126.094$ a.u. and $\alpha_{\perp} = 194.604$ a.u., and for BaF they are $\alpha_{\parallel} = 175.266$ a.u. and $\alpha_{\perp} = 288.132$ a.u.

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Conventions

In this work, atomic units (a.u.) are used. When referring to polarizability in atomic units, $1 \text{ a.u.} = 0.14818474 \text{ \AA}^3 = 1.6487773 \cdot 10^{-41} \text{ Cm}^2\text{V}^{-1}$ [1].

1 Introduction

The field of relativistic quantum chemistry has progressed fast in the last decades. Its applications include *ab initio* methods derived from the first principles of relativity and quantum mechanics, that are used to compute the energies of electronic levels in atoms and molecules [2]. These results can be used to determine the ionization potentials and electron affinities of atoms and molecules.

In this research, one striking application of these *ab initio* methods is used, which is the determination of static dipole polarizabilities of polar molecules when subjected to external electric fields. The polarizabilities of three alkaline earth monohalides will be determined: CaF, SrF and BaF. Knowledge of these quantities is needed to find the 'magic' trapping conditions for cold gases of these molecules.

1.1 'Magic' trapping conditions

As described by Kotochigova et al. [3], the use of state-insensitive light traps has many benefits for physics, in particular for precise measurements, quantum computing and the investigation of long-range molecular interactions.

In 'magic' trapping, one typically uses a red-detuned far-off-resonance optical trapping laser and an additional dc electric field to trap molecules. Polar molecules are particularly interesting, since the presence of a permanent electric dipole moment allows the shifting and mixing of levels by applying an external electric field: the ac Stark shift. For a far-off-resonance laser, the ac Stark effect can be approximated by the dc Stark effect [4].

A polar molecule can have an anisotropic dipole polarizability: the polarizability depends on the relative orientation of the molecule and the trapping laser. This can cause problems in systems where transitions between two different electronic levels have to be measured accurately: decoherence sets in quickly, making accurate measurements impossible. Fortunately, adding a dc electric field and orienting it correctly with respect to the trapping laser can help make sure that the polarizabilities of two different levels are equal, trapping the molecules for a longer period of time and allowing one to perform more accurate calculations.

1.2 The eEDM experiment

The applications of 'magic' trapping are aplenty. First and foremost, it is important to name the main motivation for this research: the experiment to find the electric dipole moment of the electron and with it, discover physics beyond the Standard Model of Particle Physics.

The electric dipole moment of the electron is small, and too small to be measured directly by current techniques, but attempts have been done at finding its upper bound. Currently, at 95% certainty level, $|d_e| \leq 0.14 \cdot 10^{-26} e \text{ cm}$ [5].

It is expected that using the 'magic' trapping setup for the state-independent trapping of SrF and BaF molecules will allow one to perform high-accuracy measurements of the electric dipole moment of the electron. This is due to the large interaction energy and strong tensor polarizability of heavy polar molecules. The effectiveness of this method has already been shown with measurements of YbF [6].

1.3 Quantum computing

A second use of trapped polar molecules is quantum computing. Computers based on quantum mechanical systems can perform calculations radically faster than classical computers, requiring far fewer components (quantum bits or 'qubits') to perform the same computations. A quantum computer has been proposed with electric dipole moments of ultracold, trapped diatomic molecules functioning as qubits [7].

These diatomic molecules would be trapped in a one-dimensional optical lattice, with one molecule at each lattice site. The qubits would be coupled via long-range electric dipole-dipole interactions. The $|0\rangle$ and $|1\rangle$ states would correspond to different rotational states of the molecule.

However, this trapping will be hindered by decoherence if the (dynamic) polarizabilities of the different rotational states are different. 'Magic' trapping removes this source of decoherence by making sure that the polarizabilities are equal through the relative orientation of the ac and dc electric field [3]. This drastically increases decoherence time, and with it, the number of calculations that can be performed.

2 Methods

2.1 Static dipole polarizability

The focus of this research is on diatomic molecules, and in particular on heteronuclear diatomic molecules, which are described by the $C_{\infty v}$ point group: rotationally symmetric around the internuclear axis, with the possibility of having a permanent electric dipole moment along that axis.

The static dipole polarizability is defined as the degree to which the charge distribution within the molecules changes due to an external electric field. Now, it is possible to define the direction of the electric field in terms of its orientation with regard to the internuclear axis (parallel, or perpendicular), and with the ab initio computational methods described in section 2.2, it is possible to determine the effect of an external electric field on the energy levels in the molecule.

For an electric field pointing along the internuclear axis of the molecule, one can find that the change in energy of the molecule consists of several components. The interaction between the permanent electric dipole moment of the molecule, and the external electric field, induces a Stark shift in the molecular energy levels: $\mathcal{E} = \mathcal{E}^0 + \mathcal{E}^E$. However, the molecule will experience polarization due to the external field, which results in an induced electric dipole moment, and hence, the energy of the molecule will depend on the external electric field up to a higher order (see equation (1) as described in [8]).

$$\mathcal{E}^{E_{\parallel}} = -\mu E_{\parallel} - \frac{1}{2}\alpha_{\parallel} E_{\parallel}^2 - \frac{1}{6}\beta_{\parallel} E_{\parallel}^3 - \frac{1}{24}\gamma_{\parallel} E_{\parallel}^4 - \dots \quad (1)$$

Here, α is the first-order dipole polarizability, and β and γ are the higher-order hyperpolarizabilities. When doing finite-field calculations in the zero-field limit, the effect of the hyperpolarizabilities is negligible and can be disregarded.

The effect of an electric field oriented perpendicularly to the internuclear axis, in contrast, is independent of the permanent electric dipole moment of the molecule. The resulting Stark shift can be seen in equation (2).

$$\mathcal{E}^{E_{\perp}} = -\frac{1}{2}\alpha_{\perp} E_{\perp}^2 - \frac{1}{24}\gamma_{\perp} E_{\perp}^4 - \dots \quad (2)$$

Where, once again, the effect of higher-order hyperpolarizabilities is neg-

ligible in the zero-field limit, and one is left with the first-order dipole polarizability.

After calculating the energies of the molecule with one of the ab initio methods described in section 2.2 while varying electric field strength and orientation, one can use a finite-field approach to find the first-order dipole polarizability. Finding α_{\perp} is relatively easy: plotting the molecular energy against the square of the electric field, one finds that $-\alpha_{\perp}$ is twice the value of the slope. Determining α_{\parallel} is a more involved process due to the presence of the $-\mu E_{\parallel}$ term. Due to the odd parity of this term, however, one can devise a consistent method to eliminate it without knowing the value of μ , by looking also at negative values for electric field strength (see equations (3) through (5)).

$$\mathcal{E}^{E_{\parallel}} = -\mu E_{\parallel} - \frac{1}{2}\alpha_{\parallel} E_{\parallel}^2 \quad (3)$$

$$\mathcal{E}^{-E_{\parallel}} = +\mu E_{\parallel} - \frac{1}{2}\alpha_{\parallel} E_{\parallel}^2 \quad (4)$$

$$\mathcal{E}^{E_{\parallel}} + \mathcal{E}^{-E_{\parallel}} = -\alpha_{\parallel} E_{\parallel}^2 \quad (5)$$

Two other quantities of interest are the average polarizability $\bar{\alpha}$, and the polarizability anisotropy $\Delta\alpha$. These are given by equations (6) and (7) [8].

$$\bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \quad (6)$$

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} \quad (7)$$

The values of α_{\parallel} , α_{\perp} , $\bar{\alpha}$ and $\Delta\alpha$ are used to correctly orient the dc electric field in the 'magic' spectroscopy setup. The goal of this research is to find a value for these polarizability quantities for the ground and first excited states of CaF, SrF and BaF molecules with a target accuracy of 10%. This is a reasonable accuracy for the ab initio methods that will be used in this work, and is a sufficient accuracy for the experimental purposes described in section 1.

2.2 Introduction to computational methods in relativistic quantum chemistry

The aim of computational methods in relativistic quantum chemistry is to find the occupation, composition and energies of atomic and molecular orbitals. To do this, many diverse methods have been developed, of which only

a few *ab initio* methods will be used in this work. They will be described in this section, along with a short summary of the parameters that influence the quality of computations: treatment of correlation, Hamiltonians and basis sets.

2.2.1 The Hartree-Fock method

The Hamiltonian of an N_e -electron molecule is given by equation (8).

$$H = \frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 - j_0 \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \frac{Z_i}{r_{ij}} + \frac{1}{2} j_0 \sum_{i \neq j}^{N_e} \frac{1}{r_{ij}}, \text{ where } j_0 = \frac{e^2}{4\pi\epsilon_0} \quad (8)$$

The Hartree-Fock approach is based on the idea that the Hamiltonian of a many-electron system can be described as the sum of all single-electron Hamiltonians. The single electrons are considered to be moving in the electrostatic field of the nuclei and the average electrostatic field of all other electrons (a so-called *self-consistent field* or SCF).

If the N_e -electron Hamiltonian is considered as the sum of N_e single-electron Hamiltonians, then the N_e -electron wave function can be considered as the product of N_e single-electron spinorbitals (position and spin eigenfunctions) numbered ϕ_a through ϕ_z , or rather as the Slater determinant in equation (9). The Slater determinant obeys the Pauli exclusion principle, which results from the antisymmetry of fermionic wave functions [2].

$$\Psi^\circ = (N_e!)^{-\frac{1}{2}} \det|\phi_a(1)\phi_b(2)\dots\phi_z(N_e)| \quad (9)$$

For closed shells with doubly occupied orbitals, the Hartree-Fock equations for the individual wave functions are:

$$f_1\psi_m(1) = \epsilon_m\psi_m(1) \quad (10)$$

f_1 is the Fock operator, which is defined in terms of the electron distribution: electrons repel each other (Coulomb repulsion) and they notice effects of spin correlation. Therefore, the Fock operator is expressed as follows:

$$f_1 = h_1 + \sum_{m'} [2J_{m'}(1) - K_{m'}(1)] \quad (11)$$

$$J_{m'}(1)\psi_m(1) = j_0 \int \psi_m^*(2) \frac{1}{r_{12}} \psi_m(1)\psi_{m'}(2) d\tau_2 \quad (12)$$

$$K_{m'}(1)\psi_m(1) = j_0 \int \psi_{m'}^*(2) \frac{1}{r_{12}} \psi_{m'}(1)\psi_m(2) d\tau_2 \quad (13)$$

As one can immediately see, the Fock operator does not only act on the wave functions, but it also depends on the electron distribution belonging to those wave functions. Therefore, one is left to solve a differential equation with many components. For each molecular orbital, an equation of the form of equation (10) has to be solved iteratively, until a certain convergence criterion is reached.

Molecular orbitals are more difficult to determine than atomic orbitals, since the latter are spherically symmetric, whereas the former are not. The LCAO-MO procedure has been developed to express molecular orbitals as linear combinations of atomic orbitals. The coefficients belonging to this linear combination have to be obtained along with the orbital energies in an iterative fashion with the Hartree-Fock approach. Finally, one is left with the total energy of the molecule and the energy of the electronic orbitals.

2.2.2 Electron correlation and the coupled-cluster method

For all the computational benefits of the Hartree-Fock approach, its largest drawback is the neglect of the effects of electron-electron correlation. Correlation is defined as the instantaneous interaction between two or more electrons. The Hartree-Fock approach gives an upper limit to the total molecular energy, the Hartree-Fock limit. The difference between the Hartree-Fock limit and the total molecular energy is called the correlation energy.

The coupled-cluster method can best be described as the decomposition of the many-electron wave function in terms of excitation amplitudes of finite-sized clusters of electrons [2][9].

One starts with a state $|\Phi\rangle$, where all levels up to the Fermi level are filled. Now, one can act on this state with operator C_2 to obtain the state $C_2|\Phi\rangle$, which corresponds to a Fermi sea with two holes, and a pair of excited electrons outside of the sea.

Multiple clusters of two electrons can be excited independently. The resulting states are given by $\frac{1}{m!} C_2^m |\Phi\rangle$, where the factor $\frac{1}{m!}$ is included in order to prevent one from counting all different indistinguishable iterations of the excited clusters. The cumulative effect of all k -tuple excitations is given by equation (14).

$$\sum_{m=0}^{\infty} \frac{1}{m!} C_k^m = e^{C_k} \quad (14)$$

Clusters of different numbers of electrons can also be excited, up to the total number of electrons in the system, N_e . The total effect of all possible orders is simply e^C , where $C = \sum_{k=1}^{N_e} C_k$, the cluster operator. Now one is left with the coupled-cluster representation of the wave function: $|\Psi\rangle = e^C |\Phi\rangle$.

In most physical cases, only single and double excitations have to be considered in order to attain an accurate results: excitations of clusters of more than two electrons have low amplitudes. In this approximation scheme, $C = C_1 + C_2$. This scheme is abbreviated by CCSD, for Coupled-Cluster Singles and Doubles. For a more accurate result, triple excitations can be considered perturbatively, resulting in the CCSD(T) approximation scheme, where (T) stands for triples. These approximation schemes drastically reduce computational time at the cost of some computational accuracy.

Another parameter that can influence computational time and accuracy, is the number of electrons that are allowed to correlate. The energies of the innermost orbitals are usually so far below the Fermi level, that excitations of the electrons in these orbitals have negligible amplitudes. Therefore, one can choose to 'freeze' these shells in order to decrease the size of the coupled-cluster matrix.

The Schrödinger equation for the coupled-cluster method is given by equation (15).

$$He^C |\Phi\rangle = Ee^C |\Phi\rangle \quad (15)$$

After some simple manipulations and the assumption that $C = C_2$ (see reference [2]), the Schrödinger equation reduces to equation (16).

$$E_{HF} + \langle \Phi | HC_2 | \Phi \rangle = E \quad (16)$$

After calculating the Hartree-Fock energy and the Hamiltonian components, the Schrödinger equation can be solved iteratively, with a start guess for the excitation amplitudes. Then, the coupled-cluster energy and wave function can be determined.

In addition to the single-reference coupled-cluster, there are also multiple multi-reference coupled-cluster methods, such as the Fock-space coupled cluster method [10], where one starts from a reference closed shell state, and

proceeds to add or remove electrons from certain 'active' orbitals, finding transition energies, ionization potentials and electron affinities.

2.2.3 Basis sets

In *ab initio* calculations, the basis set that is used, has a large influence on the computational results. A basis set contains basis functions that approximate electronic orbitals. It is impossible to use a basis set of infinite size, which means that not all configurations of the investigated atom or molecule can be accurately explored (for one, it is rather difficult to find the energies of excited states with a small basis set). A small basis set gives a large basis set truncation error, overestimating the total energy to a certain extent. However, using a large basis set drastically increases computational time. Therefore, it is important to use an appropriate basis set which contains basis functions that best approximate the atomic or molecular orbitals of the investigated species. The most widely used basis sets contain basis functions that are so-called *Gaussian-type orbitals* or GTOs. Cartesian Gaussians are functions of the form:

$$g_{ijk}(\mathbf{r}) = Nx^i y^j z^k e^{-\alpha r^2} \quad (17)$$

Where the nucleus is situated at the origin, i , j , and k are non-negative integers, N is a normalization constant and α is a positive exponent. i , j and k can take values such that $i + j + k = l$, where l is the quantum number of orbital angular momentum [2].

A minimal basis set would require one basis function for each orbital, but this would not give energies close to the Hartree-Fock limit. Therefore, increasing the basis set to a double-zeta, triple-zeta or quadruple-zeta basis set will increase computational accuracy at the cost of increasing computational time - each orbital is described by respectively two, three, or four basis functions.

For this work, two types of basis sets have been used: the first being the 'aug-cc-pVNZ' basis sets [11], which are 'correlation-consistent polarized', augmented with diffuse functions that describe the behavior of electrons far away from the nucleus. These diffuse functions are useful when computing the polarizability, since adding an external electric field will induce a net charge shift from one side of the molecule to the other, requiring a detailed description of the electronic orbitals at large radii.

The second type of basis set that has been used, are the 's-aug-dyall.vNz' basis sets [12]. These have been fitted specifically for relativistic orbitals, use N basis functions per orbital, and are augmented with diffuse functions.

2.2.4 Relativistic Hamiltonians

The choice of Hamiltonian in relativistic quantum chemistry has a significant effect on the accuracy of calculations. Relativity has a large influence on the energies of heavy elements and molecules, since by approximation (see equation 18), the velocity of an $1s$ -electron scales proportionally with the charge of the system [13][14].

$$v = Z \text{ a.u.} \approx \left(\frac{Z}{137}\right)c \quad (18)$$

Where $\frac{1}{137}$ is an approximation of the fine-structure constant α . One of the most notable effects that results from relativity, is that s - and most p -orbitals are stabilized in atoms, whereas d - and f -orbitals are destabilized. This can be explained through the fact that higher s - and p -shells penetrate the lower-lying shells more, thus 'perceiving' a higher effective nuclear charge, whereas d - and f - shells are more 'screened' from the nuclear charge by s - and p -orbitals, thus becoming destabilized [14].

An example that illustrates the significant effects of relativity on the is the computational research performed by Ahuja, Blomqvist et al. [15], which concludes that between 1.7 and 1.8 V of the 2.13 V of a lead-acid battery is the result of relativistic effects.

A second example: at -39°C , mercury has the lowest melting point of all metals [16]. This can be explained while looking at its electronic structure, which is given as $[\text{Xe}]4f^{14}5d^{10}6s^2$. Due to the high nuclear charge, the relativistic contraction of the $1s$ -shell of mercury is approximately 23%. The s -orbitals must remain orthogonal to each other, which results in contraction for the s -shells up to $6s$ [13].

In Hg, the $6s$ -shell is also filled, which means that the two $6s$ -electrons do not contribute much to bonding between mercury atoms, leaving the Hg-Hg bonds weak and lowering the melting point [14].

For this research, it is enlightening to consider the effects of relativity on the polarizability, not only for theoretical purposes, but also for computational purposes. In theoretical chemistry, knowing the effects of relativity on atomic and molecular orbitals is useful for making more accurate predictions

of the ionization potentials and other properties of heavy and super-heavy elements and molecules. Knowing the influence of relativity could indicate areas of computational improvement: if one suspects that relativistic effects are large, one could opt to include effects from quantum electrodynamics (see reference [17]) in the Hamiltonian. The reverse is also true: if one expects negligible contributions of relativity, then one could opt to use a two-component Hamiltonian instead of a four-component Hamiltonian.

In general, increased accuracy comes with increasing computational cost. Using a two-component Hamiltonian usually decreases computational time by an order of magnitude. A scalar Hamiltonian generally decreases computational time by another order of magnitude, at the cost of inaccuracy, especially for heavy systems.

The simplest relativistic Hamiltonian that can be used is the scalar Hamiltonian, which includes scalar relativistic effects, but leaves out spin-orbit coupling. In addition, there are several two-component Hamiltonians, which freeze the positronic degrees of freedom and allow for fine-structure spin-orbit coupling energies to be taken into account. The energies computed with two-component Hamiltonians are always slightly different from those computed with four-component Hamiltonians, but in more recent years, the X2C (exact two-component) Hamiltonian has been developed, which gives very accurate results in most cases [18].

To fully include the effects of relativity on a system, one must use the four-component Dirac Hamiltonian, which is a matrix operator which takes into account the existence of the positron in addition to the electron, and also describes spin states [19].

In equation form, the Dirac Hamiltonian for an electron in a molecular field is given by (19).

$$h_D = \beta' mc^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p}) + V = \begin{bmatrix} V & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - 2mc^2 \end{bmatrix} \quad (19)$$

Where $V = q\phi$ is the energy due to the nuclear electrostatic potential ϕ and $\boldsymbol{\alpha}$ is the vector containing all Pauli matrices σ_x , σ_y and σ_z . In explicit matrix form, the Dirac Hamiltonian looks as follows:

$$\begin{pmatrix} q\phi & 0 & cp_z & c(p_x - ip_y) \\ 0 & q\phi & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & -2mc^2 + q\phi & 0 \\ c(p_x + ip_y) & -cp_z & 0 & -2mc^2 + q\phi \end{pmatrix} \quad (20)$$

This is the one-electron part of the Hamiltonian. In addition, there are two-electron contributions to the Hamiltonian: the first being the non-relativistic Coulomb repulsion between electrons and the second being the relativistic Breit operator as seen in reference [17], which describes spin-spin and spin-other-orbit interactions. This last operator often complicates calculations and is therefore left out in the Dirac-Coulomb Hamiltonian.

2.3 The DIRAC Program

The methods described in the previous paragraphs, are performed with the computational package DIRAC, or Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations [20]. The program was run on the Peregrine HPC cluster of the University of Groningen.

3 Results

To ascertain the validity of the results attained in this research, first the results of the coupled-cluster method have to be compared to other computational methods and experimental values. This will be done for the beryllium atom (Be) and the magnesium monohydride (MgH) and fluorine molecules (F_2). Subsequently, the polarizabilities of calcium monofluoride (CaF), strontium monofluoride (SrF) and barium monofluoride (BaF) will be calculated.

3.1 The beryllium atom

There is a wide range of computational results for the polarizability of the beryllium atom. Since the beryllium atom is rotationally symmetric, there is no difference between components of its polarizability ($\alpha_{\parallel} = \alpha_{\perp}$).

With the results of the finite-field method, one can find the following polarizabilities for different methods, Hamiltonians and basis sets (all values in atomic units):

		SCF	CCSD	CCSD(T)
aug-cc-pVDZ	4C	45.336	37.846	37.780
aug-cc-pVTZ	4C	45.682	38.018	37.928
aug-cc-pVQZ	4C	45.830	38.182	38.044
aug-cc-pVQZ	X2C	45.832	38.184	38.046
aug-cc-pVQZ	NR	45.858	38.200	38.062

In previous work, the polarizability of beryllium was found to be 37.80 a.u. with the relativistic coupled-cluster approach [21]. The CCSD(T) value of 38.044 a.u. obtained in this work differs by only a few tenths of an atomic unit. This may result from the Hamiltonian that is used, the treatment of higher-order correlation, or the use of basis set.

One can see that the effects of relativity are nearly negligible (a few hundredths of an atomic unit): as a result of the small nuclear charge of beryllium, the electrons move at a negligible fraction of light speed. However, correlation has a large influence on the polarizability: nearly 20%. The basis set has an influence of around 1%, which can also be attributed to its small size.

3.2 The magnesium monohydride molecule

In previous calculations of the static dipole polarizabilities of magnesium monohydride [8], the reported polarizabilities are:

	SCF	CCSD	CCSD(T)
α_{\parallel}	54.99	58.22	58.47
α_{\perp}	69.63	68.77	68.75
$\bar{\alpha}$	64.76	65.26	65.33
$\Delta\alpha$	-14.65	-10.56	-10.29

The magnesium monohydride molecule contains 13 electrons, of which 12 are in closed shells, and 1 is in an open shell. For the purpose of 'freezing' low-energy orbitals, two electrons are in an orbital with energy lower than -20.0 a.u., which means that they can be disregarded in the coupled-cluster calculations. Now, the following polarizabilities are obtained:

α_{\parallel}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	55.528	59.521	59.986
s-aug-dyall.v3z	X2C	55.060	58.606	59.119
s-aug-dyall.v4z	X2C	55.091	58.557	59.071
s-aug-dyall.v2z	NR	54.761	58.691	59.159

α_{\perp}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	69.916	66.858	66.786
s-aug-dyall.v3z	X2C	69.592	66.590	66.480
s-aug-dyall.v2z	NR	69.512	66.444	66.356

Notable is the fact that polarizabilities decrease with an increasing basis set size. Intuitively, this should not occur, since increasing the basis set size should also increase the number of higher, unoccupied orbitals that electrons can be excited into. However, the results do converge with respect to the basis set, at values close to those reported in reference [8].

From these results, one can obtain the average polarizability using equation (6). $\bar{\alpha}$ is as follows:

$\bar{\alpha}$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	65.120	64.412	64.519
s-aug-dyall.v3z	X2C	64.748	63.929	64.026
s-aug-dyall.v2z	NR	64.595	63.860	63.957

Finally, the polarizability anisotropy $\Delta\alpha$ was found to be:

$\Delta\alpha$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	-14.388	-7.337	-6.800
s-aug-dyall.v3z	X2C	-14.532	-7.984	-7.361
s-aug-dyall.v2z	NR	-14.751	-7.753	-7.197

3.3 The fluorine molecule

In addition to computational results, there are also experimental results available for the polarizability of the fluorine molecule. Therefore, it is useful to compare the results obtained by the coupled-cluster method with these experimental results to validate the accuracy of the method.

The experimental value of the average polarizability of F_2 is $\bar{\alpha} = 1.43 \cdot 10^{-40} \text{ Cm}^2\text{V}^{-1} = 8.673 \text{ a.u.}$ [22]. There is no experimental value available for the polarizability anisotropy, but in principle, the average polarizability should be enough to verify the accuracy of the coupled-cluster method.

For the ab initio calculations, an experimental value was used for R_e , the internuclear distance. This value is $R_e = 1.4131 \pm 0.008 \text{ \AA}$ [23].

The fluorine molecule contains 18 electrons, of which 14 have an energy higher than -20.0 atomic units. The remaining 4 electrons are disregarded in the coupled-cluster calculations. The following results are found:

α_{\parallel}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	14.171	11.717	11.759
s-aug-dyall.v3z	X2C	14.522	12.196	12.223
s-aug-dyall.v4z	X2C	14.566	12.256	12.274

α_{\perp}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	4.820	5.320	5.394
s-aug-dyall.v3z	X2C	5.454	6.112	6.234

Then, $\bar{\alpha}$ is found to be the following:

$\bar{\alpha}$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	7.937	7.452	7.516
s-aug-dyall.v3z	X2C	8.477	8.140	8.230

Comparing the CCSD(T) value of 8.230 a.u. to the experimental value of 8.673 a.u., one can see that the ab initio methods provide an accurate way to obtain the polarizability of a diatomic molecule. Rather notable is the fact that increasing the size of the basis set from triple-zeta to quadruple-zeta has only marginal effects on the polarizability, which is something that needs to be taken into account when calculating the polarizabilities of heavier molecules, in the case computational resources are scarce. However, there is a significant difference between the polarizabilities obtained with the s-aug-dyall.v2z and s-aug-dyall.v3z basis sets.

3.4 The calcium monofluoride molecule

The CaF molecule contains 29 electrons, of which 4 are in orbitals with energies below -20.0 atomic units. Therefore, only 25 electrons are considered in the coupled-cluster calculations. For the internuclear distance, the experimental value of $R_e = 1.97 \text{ \AA}$ is used [24]. Now, the computational results are:

α_{\parallel}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	97.214	93.728	94.566
s-aug-dyall.v3z	X2C	99.057	95.630	96.441
s-aug-dyall.v4z	X2C	101.284	98.258	99.241
s-aug-dyall.v2z	NR	97.001	93.533	94.339
α_{\perp}				
s-aug-dyall.v2z	X2C	174.856	147.262	145.982

$\bar{\alpha}$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	148.975	129.417	128.843
$\Delta\alpha$				
s-aug-dyall.v2z	X2C	-77.642	-53.534	-51.416

For the parallel polarizability, one can see that convergence is not yet reached with respect to the basis set. This can be the result of the size of the system. It could be that further augmentation of the basis set is needed in order to reach a sufficient convergence with respect to the basis set. The effects of relativity and correlation on this system are relatively small when compared to the influence of the basis set. As intuitively expected, the parallel polarizability does increase with the basis set.

Unfortunately, there were not enough computational resources and time to calculate the perpendicular component of the polarizability of SrF with a basis set larger than s-aug-dyall.v2z.

3.5 The strontium monofluoride molecule

The SrF molecule contains 47 electrons, of which 12 are in orbitals of energy lower than -20.0 a.u., and therefore only 35 electrons are considered in the coupled-cluster calculations. The experimental value of $R_e = 2.08 \text{ \AA}$ is used for the internuclear distance [24]. The following computational results are obtained:

α_{\parallel}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	138.488	124.907	125.319
s-aug-dyall.v3z	X2C	141.029	126.437	126.241
s-aug-dyall.v4z	X2C	141.313	126.408	126.094
α_{\perp}				
s-aug-dyall.v2z	X2C	252.996	197.776	194.604

$\bar{\alpha}$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	214.827	173.486	171.509
$\Delta\alpha$				
s-aug-dyall.v2z	X2C	-114.508	-72.869	-69.285

Here, the effect of correlation on the polarizabilities is significant: it is over 25% for the perpendicular component of the polarizability. For the parallel component, the calculations converge with respect to the basis set.

Once again, due to limited time and computational resources, the perpendicular component of the polarizability of SrF could not be calculated with a basis set larger than s-aug-dyall.v2z.

3.6 The barium monofluoride molecule

The BaF molecule contains 65 electrons, of which 30 are in orbitals of energy lower than -20.0 atomic units, and thus only 35 electrons are considered in the coupled-cluster approach. The experimental value of $R_e = 2.16 \text{ \AA}$ is used for the internuclear distance [24]. The following results are found:

α_{\parallel}		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	214.365	178.219	176.826
s-aug-dyall.v3z	X2C	213.482	176.803	174.011
s-aug-dyall.v4z	X2C	220.408	179.187	175.266
α_{\perp}				
s-aug-dyall.v2z	X2C	417.254	297.062	288.132

$\bar{\alpha}$		SCF	CCSD	CCSD(T)
s-aug-dyall.v2z	X2C	349.624	257.448	251.030
$\Delta\alpha$				
s-aug-dyall.v2z	X2C	-202.889	-118.843	-111.306

The value of the parallel component of the polarizability does not vary much with respect to the basis set. However, the SCF value with the s-aug-dyall.v4z basis set does not appear to be correct, since it differs a lot from the previous values.

Also for BaF, there were not enough computational resources and time available to complete the calculations of the perpendicular component of the polarizability with larger basis sets than s-aug-dyall.v2z.

Notable is the especially large negative polarizability anisotropy of BaF, which indicates a large orientation-dependence when inserted into an external electric field.

4 Discussion

In this research, it was first shown that computational results from previous work could be reproduced with the coupled-cluster method described in section 2.2.2. Moreover, the method yields results consistent with experimental results of F_2 , as was shown in section 3.3. It is thus possible to apply the coupled-cluster method to the calculation of static dipole polarizabilities of molecules.

Subsequently, accurate values were determined for the polarizabilities of CaF, SrF and BaF, up to the accuracy of the ab initio methods that were used. However, before the results of this work can be applied to experimental research as described in section 1, several actions are still required. A brief clarification will be given for each of these steps.

4.1 Perpendicular polarizability components

First and foremost, to get a better grasp on the value of the polarizability anisotropy of the molecules in question, higher-accuracy calculations must be done on the perpendicular components of the polarizabilities. The largest hurdles in performing these calculations, were the time limitations and limited availability of computational resources for these high-memory computations. With an increased timeframe, it should be possible to obtain more accurate results for the perpendicular components of polarizability and thus the polarizability anisotropy. Then, the behavior of the molecules in question in an optical trapping field can be more accurately predicted.

4.2 Excited states

To find out the correct trapping conditions, the polarizabilities of the $A\ ^2\Pi_r$ excited states of CaF, SrF and BaF must also be known. To find these values, one has to consider using the Fock-space coupled-cluster method. Starting from the singly ionized closed-shell BaF^+ molecule, one can allow one electron to go into several levels above the Fermi level, which can be the level corresponding to the $X\ ^2\Sigma^+$ ground state, the $A\ ^2\Pi_r$ excited state, or some other excited state. Now, after identifying the energy level belonging to the $A\ ^2\Pi_r$ state, one can use the finite-field method to find the polarizability of this excited state.

5 Closing remarks

Hopefully, the results found in this work will be useful and enlightening to the reader. It is to be hoped that the knowledge of the polarizabilities of the molecules studied in this work will be used to further our understanding of physics beyond the Standard Model.

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