Multipole polarizabilities and long-range interactions of the fluorine atom

O. Zatsarinny* and K. Bartschat

Department of Physics, Drake University, Des Moines, IA, USA

J. Mitroy† and J.-Y. Zhang

Faculty of Technology, Charles Darwin University, Darwin NT 0909, Australia

(Dated: February 23, 2009)

Abstract

The polarizabilities of the ground state of fluorine are determined by the box-based $B$-spline configuration-interaction method. The ground-state static and tensor polarizabilities are calculated as $\alpha_d = 3.49 \, a_0^3$ and $\alpha_2 = 0.303 \, a_0^3$, respectively. The resulting excitation matrix elements are employed to compute the inter-atomic dispersion interactions for the HF and F$_2$ molecules.

PACS numbers: 31.15.A-, 31.15.ag, 34.20.Cf.

*Electronic address: oleg_zoi@yahoo.com
†Electronic address: jxm107@rsphysse.anu.edu.au
I. INTRODUCTION

In recent years there has been increased interest in describing the long-range behavior of inter-atomic potential curves. One motivation has undoubtedly been the explosive development of the field of cold-atom physics. Areas of investigation include the formation of quantum degenerate gases [1–3], the development of optical frequency standards [4, 5], quantum computation [6], the use of atoms for studying fundamental physics [7], and the formation of cold molecules [8]. Consequently, it has become increasingly important to know the asymptotic part of the potential curves for many atomic pairs. For example, the dispersion coefficients form the bridge between the binding energy of the least-bound ro-vibrational levels to the prediction of the scattering length [9], which is the most important parameter in characterizing the behavior of quantum degenerate gases.

Independently of these developments in physics, there has been increased interest from the chemistry community in developing models of inter-atomic potentials from the minimum of the potential surface to asymptotic distances. As spectroscopic descriptions of diatomic spectra increase in accuracy, yielding ever more precise potential curves, there is also a complementary desire to increase the range over which the potentials are valid. The well-known Rydberg-Klein-Rees (RKR) method is essentially an inversion procedure to create a pointwise potential surface. However, the fact that the resulting potential surface is local in extent has some disadvantages [10]. Accordingly, the direct-potential-fit (DPF) approach is of increasing interest [10–15]. The DPF method characterizes the interaction potential over the complete radial range using functional forms with a finite number of parameters. Most recently, Le Roy and Henderson [16] developed functional forms designed to evolve into the correct asymptotic form at long distances from the atom.

The hydrogen-fluoride molecule is a good candidate for a direct-potential-fit, since the ro-vibrational spectrum is known in great detail [17–19]. Unfortunately, there is no precise information available about the long-range part of the H-F potential.

The present work generates a pseudo-excitation spectrum for the fluorine atom using a $B$-spline configuration-interaction (CI) calculation as its cornerstone. The resulting lists of matrix elements are subsequently used to compute the hydrogen-fluoride dispersion coefficients. The present work shares similarities with earlier efforts by Meath and collaborators, who developed pseudo-oscillator-strength distributions for a number of systems [20–23]. One
difference from the work of Meath and collaborators is that the present method generates lists of reduced matrix elements rather than oscillator strengths. While oscillator strength distributions can be used to generate parts of the dispersion interaction, reduced matrix elements are required for its complete description.

The only previous estimation of the hydrogen-fluoride dispersion coefficients originate from a calculation that was not described in detail [18]. However, there have been a number of calculations of the fluorine ground-state polarizabilities at varying levels of sophistication [24–32]. These calculations can be used to both validate and fine-tune the lists of reduced matrix elements from the $B$-spline CI calculation.

The dispersion coefficients of the $F_2$ inter-atomic potential were also computed. The potential curve for this molecule has recently been the subject of a very refined theoretical analysis [33–35]. The long-range $C_6$ dispersion coefficient from Chu and Dalgarno [36] was incorporated into the analysis. However, the Chu and Dalgarno value of $C_6$ only considered the spherically symmetric part of the interaction. The present analysis, on the other hand, accounts for the anisotropic nature of the interaction and also gives the $C_8$ and $C_{10}$ dispersion coefficients.

II. METHODOLOGY OF CALCULATION

A. Overview of van der Waals interaction calculation

The long-range van der Waals interaction between two atoms in $S$-states with an internuclear separation of $R$ can be written as [37, 38]

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots .$$  (1)

The $C_n$ parameters are the dispersion coefficients. An additional term is present when both atoms are in a state with the orbital angular momentum, $L$ greater than zero. For two states with $L = 1$, for example, this additional term is given by [39, 40]

$$V_{QQ} = -\frac{C_5}{R^5} .$$  (2)

Our approach to generate the dispersion coefficients is based on the use of sum rules [37–39, 41]. This reduces the calculation of the $C_n$ parameters for two spherically symmetric
atoms to summations over the products of the absorption oscillator strengths (originating in the ground state) divided by an energy denominator. The sums should include contributions from all discrete and continuum excitations. In practice a pseudo-state representation is used, which gives a discrete representation of the continuum [39, 42, 43]. The sum over oscillator strengths needs to be rewritten in terms of a sum over the reduced matrix elements of the electric multipole operator in cases where one (or both) of the atoms is in a state with \( L > 0 \) [39, 41].

The major part of any numerical treatment involves the generation of the lists of reduced transition matrix elements for the two atomic states. This requires lengthy calculations to generate the excitation spectrum of the pseudo-state representation. It is then a relatively straightforward effort to use the procedures outlined in previous works [39, 41] to process the lists of matrix elements and generate the dispersion coefficients.

**B. The CI calculations of the F states**

The calculations of fluorine bound states are complicated by several factors. First, the outer orbitals in the \( 2s^22p^4nl \) configurations exhibit a strong term dependence. Second, there is strong configuration mixing between the \( 2s^22p^4ns \) and \( 2s^22p^4nd \) series, built upon different parent terms \( 2s^22p^4 \, ^4S^e, \, ^2D^e \) and \( ^2P^e \). Further complications arise from the inner-core correlation. These effects are treated by employing the \( B \)-spline box-based close-coupling method described by Zatsarinny and Froese Fischer [44] and programmed by Zatsarinny [45].

In this method, the atomic wave function describing the total \((N + 1)\)-electron system is expanded in terms of products of \( N \)-electron parent states and the radial functions for the outer electron, which in turn are expanded in a \( B \)-spline basis. The close-coupling expansion
of the fluorine Rydberg series is represented by the schematic form

\[
\Phi(LS) = A \sum_{ij, L'S'} a_{ij} \{\varphi(2s^22p^4; L'S') \cdot B_i(r)|l_j s\}\}^{LS} \\
+ A \sum_{ij, L'S'} b_{ij} \{\varphi(2s2p^5; L'S') \cdot B_i(r)|l_j s\}\}^{LS} \\
+ A \sum_{ij} c_{ij} \{\varphi(2s^22p^33s\,1P) \cdot B_i(r)|l_j s\}\}^{LS} \\
+ A \sum_{ij} d_{ij} \{\varphi(2p^6\,1S) \cdot B_i(r)|l_j s\}\}^{LS} \\
+ \delta_{L,1}\chi(2s^22p^5\,2P)
\]  

Here the B-splines \(B_i(r)\) represent the radial part of the outer orbitals while \(|l_j s\) denotes the spin-angular part of the one-electron functions. The operator \(A\) includes antisymmetrization and implies that the parent function \(\varphi\) is coupled to the outer electron, according to the usual angular momentum rules, to form a state with total term \(LS\) and well-defined parity.

The first two sums in this expansion represent all the single-electron excitations from the \(2s^22p^5\) ground state. The next two sums were introduced to guarantee the completeness of Eq. (3) due to strong configuration mixing of the \(2s^22p^4\,1S^o\) and \(2s^22p^5\,1P^o\) parent states with the \(2p^6\,1S^o\) and \(2s^22p^33s\,1P^o\) states, respectively. Finally, the multi-configuration expansion \(\chi(2s^22p^5\,2P^o)\) for the ground states was added to Eq. (3) explicitly to allow for an extensive description of short-range correlations in this state.

All the \(\varphi\) and \(\chi\) states in Eq. (3) were constructed from multi-configuration Hartree-Fock (MCHF) expansions. The configuration expansions for each state contained the principal configuration along with all one-electron and two-electron excitations from the \(2s\) and \(2p\) subshells to the set of correlation functions \(nl\) \((l = 0 - 3)\), which are specific for inner-core correlation. The latter were generated using the MCHF program of Froese Fischer and collaborators \[46\]. Each core state (as well as the ground state \(2s^22p^5\,2P^o\)) was generated with fully term-dependent orbitals, since this vastly improves the convergence of the multi-configuration expansions.

The unknown functions for the outer valence electron were expanded in the \(B\)-spline basis and the corresponding equations were solved subject to the condition that the wave functions vanish at the boundary. The details of this procedure are given in \[44\]. The choice of \(B\)-splines as basis functions has many advantages. First of all, choosing a sufficiently large box and an appropriate knot sequence results in a set of \(B\)-splines that form an effectively
complete basis for the solutions of the one-electron Hamiltonian. The completeness of the $B$-spline basis ensures that, in principle, we can study the entire Rydberg series, whereas the multi-channel form (3) allows us to include explicitly the interaction between different Rydberg series. The radial functions of the valence electrons were chosen to be orthogonal to the $2s$ and $2p$ electron but not to the correlation orbitals. This avoids the need to introduce additional compensation configurations into Eq. (3).

The above scheme yields non-orthogonal, term-dependent sets of valence orbitals for each $LS$ term. The number of physical states that can be generated in this method depends upon the size of the $R$-matrix box. Choosing $R_{\text{box}} = 50 \, a_0$ (where $a_0 = 0.529177 \times 10^{-10}$ m is the Bohr radius) yields a good description for all low-lying states of F up to $n = 6$. Along with these physical states, the above scheme also provides a set of pseudo-states, with the lowest states representing the remaining bound states and the rest representing the continuum. The number and density of pseudo-states depend on the size of the $B$-spline basis. A semi-logarithmic grid of knots [44], with a maximum step size of $1 \, a_0$ was used. The resulting $B$-spline basis consisted of 95 splines of order 8. The completeness of the $B$-spline basis was checked by calculations of the ground-state polarizability with different numbers of $B$-splines. The polarizability was found to be stable against any further increase in the number of $B$-splines.

The calculations of the transition matrix elements were carried out with the program BSR_DMAT which is part of the BSR complex [45]. This program needed to be extended to higher multipoles. This program allows for the use non-orthogonal orbitals for both the initial and final states, thus permitting a good description of relaxation effects.

III. FLUORINE EXPECTATION VALUES

A. Energy levels

The ability of the present semi-empirical CI calculation to reproduce the low-lying spectrum can be assessed from Table I. There is a tendency for the excitation energies to be between 0.001 and 0.007 a.u. larger than the experimental values. The discrepancy between theory and experiment is largest for the lowest two excited states, but no particular significance should be attached to this.
TABLE I: Theoretical and experimental energy levels (in hartree) of some low-lying doublet states of the F atom. The energies are given relative to the energy of the ground state. The experimental energies (taken from [47]) states are spin-orbit averages with the usual \((2J + 1)\) weighting factors.

<table>
<thead>
<tr>
<th>State</th>
<th></th>
<th>B-spline CI</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2p^5 2p^o)</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(2p^4(3P^e)3s 2P^e)</td>
<td>0.483071</td>
<td>0.476950</td>
<td></td>
</tr>
<tr>
<td>(2p^4(1D^e)3s 2D^e)</td>
<td>0.570311</td>
<td>0.563401</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)4s 2P^e)</td>
<td>0.576750</td>
<td>0.575065</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)3d 2D^e)</td>
<td>0.584537</td>
<td>0.582840</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)3d 2F^e)</td>
<td>0.585136</td>
<td>0.584231</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)3d 2P^e)</td>
<td>0.585676</td>
<td>0.584645</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)3p 2D^o)</td>
<td>0.538052</td>
<td>0.535385</td>
<td></td>
</tr>
<tr>
<td>(2p^4(3P^e)3p 2P^o)</td>
<td>0.543609</td>
<td>0.540909</td>
<td></td>
</tr>
</tbody>
</table>

B. Dipole transitions from the ground state

A further assessment of the CI calculations comes from the tabulation of multiplet strengths in Table II. The absorption oscillator strength for a multipole transition from \(g \rightarrow n\), with an energy difference of \(\Delta E_{ng} = E_g - E_n\), is defined as

\[
f^{(k)}_{gn} = \frac{2S^{(k)}_{gn} \Delta E_{ng}}{(2k + 1)(2L_g + 1)}.
\]

In this expression, \(L_g\) is the orbital angular momentum of the initial state while \(k\) is the polarity of the transition (note, there are other definitions of the oscillator strength that give different numerical values for \(k \geq 2\) [49]). The multiplet strength, \(S^{(k)}_{gn}\), is the square of the reduced matrix element,

\[
S^{(k)}_{gn} = |\langle \psi_g; L_g \parallel r^k C^k (\hat{r}) \parallel \psi_n; L_n \rangle|^2.
\]

Table II gives the lines strengths for some of the low-lying transitions from the \(2P^o\) ground state. The line strengths for individual \(J\) components are derived from the multiplet strengths through multiplication by the appropriate recoupling coefficients. Line strengths
different states. Levels and the spin-orbit interaction leads to mixing of the transition strength amongst the respective recoupling coefficients. There are a large number of closely spaced energy excitations. Making a meaningful comparison is more complicated for transitions to higher-lying excited states.

### TABLE II: Line strengths for dipole transitions between the ground state and some low-lying excited states.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Present CI</th>
<th>MCHF [48]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(3P^e)3s , ^2P^e_{1/2}$</td>
<td>0.3945</td>
<td>0.4081</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(3P^e)3s , ^2P^e_{3/2}$</td>
<td>0.1973</td>
<td>0.2007</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)3s , ^2P^e_{1/2}$</td>
<td>0.1973</td>
<td>0.2062</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)3s , ^2P^e_{3/2}$</td>
<td>0.9864</td>
<td>1.0280</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(1D^e)3s , ^2D^e_{3/2}$</td>
<td>0.2550</td>
<td>0.2761</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(1D^e)3s , ^2D^e_{3/2}$</td>
<td>0.0510</td>
<td>0.0502</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(1D^e)3s , ^2D^e_{5/2}$</td>
<td>0.4590</td>
<td>0.4864</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(3P^e)4s , ^2P^e_{1/2}$</td>
<td>0.0617</td>
<td>0.0458</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(3P^e)4s , ^2P^e_{3/2}$</td>
<td>0.0309</td>
<td>0.0210</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)4s , ^2P^e_{1/2}$</td>
<td>0.0309</td>
<td>0.0235</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)4s , ^2P^e_{3/2}$</td>
<td>0.1543</td>
<td>0.1049</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{1/2} \rightarrow 2p^4(3P^e)3d , ^2D^e_{3/2}$</td>
<td>0.1076</td>
<td>0.0504</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)3d , ^2D^e_{3/2}$</td>
<td>0.0215</td>
<td>0.0394</td>
</tr>
<tr>
<td>$2p^5 , ^2P_{3/2} \rightarrow 2p^4(3P^e)3d , ^2D^e_{5/2}$</td>
<td>0.1937</td>
<td>0.1619</td>
</tr>
</tbody>
</table>

The current CI line strengths for the $2p^5 \, ^2P^o \rightarrow 2p^4(3P^e)3s \, ^2P^e$ transitions are slightly smaller than the MCHF values. The same is true for the $2p^5 \, ^2P^o \rightarrow 2p^4(1D^e)3s \, ^2D^e$ transitions. Making a meaningful comparison is more complicated for transitions to higher-lying levels such as $2p^4(3P^e)3d \, ^2D^e$. The MCHF calculations show individual line strengths for the various fine-structure components deviating considerably from the ratios expected from the respective recoupling coefficients. There are a large number of closely spaced energy levels and the spin-orbit interaction leads to mixing of the transition strength amongst the different states.
TABLE III: The polarizabilities for the ground state of fluorine. Definitions of the polarizabilities are given in the text. Polarizabilities obtained by a number of other groups are also listed.

<table>
<thead>
<tr>
<th>Calculation Type</th>
<th>Polarizability type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$-Spline CI (Present)</td>
<td>$\alpha_d$</td>
<td>3.490</td>
</tr>
<tr>
<td>CEPA-NO [24]</td>
<td>$\alpha_d$</td>
<td>3.759</td>
</tr>
<tr>
<td>CCSD(T) [50]</td>
<td>$\alpha_d$</td>
<td>3.70</td>
</tr>
<tr>
<td>CASPT2 [30]</td>
<td>$\alpha_d$</td>
<td>3.76</td>
</tr>
<tr>
<td>CASPT2 [31]</td>
<td>$\alpha_d$</td>
<td>3.73</td>
</tr>
<tr>
<td>CI [29]</td>
<td>$\alpha_d$</td>
<td>3.71</td>
</tr>
<tr>
<td>RCI (actual) [26]</td>
<td>$\alpha_d$</td>
<td>3.71</td>
</tr>
<tr>
<td>RCI (corrected) [26]</td>
<td>$\alpha_d$</td>
<td>3.44</td>
</tr>
<tr>
<td>DFT [36]</td>
<td>$\alpha_d$</td>
<td>3.4</td>
</tr>
<tr>
<td>MCSCF [28]</td>
<td>$\alpha_d$</td>
<td>3.15</td>
</tr>
<tr>
<td>HF [25]</td>
<td>$\alpha_d$</td>
<td>3.5</td>
</tr>
<tr>
<td>QDT-GF [27]</td>
<td>$\alpha_d$</td>
<td>2.95</td>
</tr>
<tr>
<td>$B$-Spline CI (Present)</td>
<td>$\alpha_2$</td>
<td>0.303</td>
</tr>
<tr>
<td>CEPA-NO [24]</td>
<td>$\alpha_2$</td>
<td>0.293</td>
</tr>
<tr>
<td>CASPT2 [30]</td>
<td>$\alpha_2$</td>
<td>0.32</td>
</tr>
<tr>
<td>CCSD(T) [50]</td>
<td>$\alpha_2$</td>
<td>0.28</td>
</tr>
<tr>
<td>$B$-Spline CI (Present)</td>
<td>$\alpha_q$</td>
<td>12.24</td>
</tr>
<tr>
<td>CEPA-NO [32]</td>
<td>$\alpha_q$</td>
<td>12.69</td>
</tr>
<tr>
<td>$B$-Spline CI (Present)</td>
<td>$\alpha_o$</td>
<td>88.43</td>
</tr>
</tbody>
</table>

C. Polarizabilities

Table III reports the static dipole, quadrupole, and octupole polarizabilities for the F ground state. While there have been a number of calculations of the dipole polarizability, to our knowledge there has only been one other calculation for the quadrupole polarizability [32] and none for the octupole polarizability. Due to its $^2\text{P}^o$ symmetry, the ground state also has a tensor polarizability for the dipole excitation.

The static dipole polarizability in terms of excitations to $^2\text{S}^e$, $^2\text{P}^e$ and $^2\text{D}^e$ states is defined
as
\[
\alpha_d = \sum_{n, L_n=0} f_{0n}^{(1)} \epsilon_{0n}^2 + \sum_{n, L_n=1} f_{0n}^{(1)} \epsilon_{0n}^2 + \sum_{n, L_n=2} f_{0n}^{(1)} \epsilon_{0n}^2.
\] (6)

This polarizability is the average of the \(M\)-dependent polarizabilities
\[
\alpha_d = \frac{\alpha_{d,0} + \alpha_{d,1} + \alpha_{d,-1}}{3}.
\] (7)

The scalar part of the quadrupole (\(\alpha_q\)) and octupole (\(\alpha_o\)) polarizabilities can be computed by expressions similar to Eq. (6) with the appropriate \(k\)-pole oscillator strength.

It is common to use the tensor polarizability to relate the \(M\)-dependent polarizabilities to the static polarizability. The tensor polarizability for a state with \(L = 1\) is defined as [51–53]
\[
\alpha_2 = -\sum_{n, L_n=0} f_{0n}^{(1)} \epsilon_{0n}^2 + \frac{1}{2} \sum_{n, L_n=1} f_{0n}^{(1)} \epsilon_{0n}^2 - \frac{1}{10} \sum_{n, L_n=2} f_{0n}^{(1)} \epsilon_{0n}^2.
\] (8)

With this definition, one obtains
\[
\alpha_{d,0} = \alpha_d - \alpha_2;
\] (9)
\[
\alpha_{d,\pm1} = \alpha_d + \frac{1}{2} \alpha_2.
\] (10)

Table III lists calculated polarizabilities from a number of sources. There is a noticeable tendency for the more sophisticated correlation-type calculations to yield \(\alpha_d\) values between 3.70 and 3.76 a.u. and these two limits should be regarded the best estimates of the theoretical uncertainties. The CI variation-perturbation calculation gives 3.71 a.u. [29]. The coupled electron-pair approximation calculation using pseudo-natural orbitals (CEPA-PNO) yields 3.759 a.u. [24]. A coupled-cluster calculation treating single and double excitations explicitly and triple excitations perturbatively CCSD(T) predicts 3.70 a.u. [50]. The complete active-space perturbation theory (CASPT2) first constructs a CI wave function as a reference state for a perturbative treatment [30, 31]. The two independent CASPT2 calculations gave 3.73 and 3.76 a.u. for \(\alpha_d\). A large relativistic configuration-interaction (RCI) calculation by Fleig and Sadlej gave a dipole polarizability of 3.71 a.u. [26]. However, the authors infer that including the contributions from missing configurations reduced the polarizability to 3.44 a.u. This reduction is hard to justify in the absence of a validation on a related system such as the neon atom. It should be noted that the CI, CEPA-PNO, and CCSD(T) methods have also been applied to the determination of the neon dipole polarizability [24, 29, 54], giving values within 1-2% of the experimental result [55].
Table III also lists polarizabilities computed using density functional theory (DFT) [36], an uncoupled Hartree-Fock (UHF) approximation [25], a small multi-configuration self-consistent field (MCSCF) calculation [28], and a quantum defect theory approach QDT-GF [27]. However, these calculations are not expected to yield polarizabilities as accurate as those mentioned in the previous paragraph.

The present calculation predicts a tensor polarizability of 0.303 a.u. This small value is compatible with the other values listed in Table III. There is also reasonable agreement between the present quadrupole polarizability of 12.24 and the PNO-CEPA value of 12.69 a.u. [32].

IV. THE DISPERSION COEFFICIENTS

A. The 1s\(^2\) core oscillator strength distribution

The contribution of the 1s\(^2\) core to the dispersion coefficients was incorporated by making a pseudo-oscillator strength distribution for the core. Initially, a CI calculation of the F\(^{7+}\) polarizability was made giving a value of 0.00162 a.u.. In addition the oscillator strength sum rule \(S(-1)\) (the sum rule with an energy denominator raised to a power of 1 [23, 42, 56]) was evaluated giving 0.0535 a.u. Using these two sum rules as constraints, the core pseudo-oscillator strength distribution, \((f_{\text{core},i}, \Delta E_{\text{core},i})\), was constructed with two terms as (1.0, 58.54) and (1.0, 27.44) The mechanics of including the core into the evaluation of the dispersion constants was described previously [39, 42].

B. Hydrogen fluoride

The calculation of the dispersion coefficients is reduced to a purely mechanical calculation once the set of reduced matrix elements has been generated [39, 41, 57]. The reduced matrix element set for hydrogen was produced by diagonalizing the hydrogen Hamiltonian in a basis of 15 Laguerre-type orbitals. The resulting list of hydrogen reduced matrix elements may be regarded as close to exact for the purpose of generating the dispersion coefficients [58, 59].

The dispersion coefficients between F(2p\(^5\)) and H(1s) states are listed in Table IV. Dispersion coefficients are given to molecules in both \(\Sigma\) and \(\Pi\) states. The dispersion coefficients are slightly larger for the \(\Pi\) states. The influence of the core on the dispersion coefficients
TABLE IV: The dispersion coefficients (in atomic units) for the HF ground state.

<table>
<thead>
<tr>
<th>System</th>
<th>$C_6$ (a.u.)</th>
<th>$C_8$ (a.u.)</th>
<th>$C_{10}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma$</td>
<td>6.417</td>
<td>121.7</td>
<td>2946</td>
</tr>
<tr>
<td>$\Sigma$ (scaled)</td>
<td>6.589</td>
<td>123.5</td>
<td>2977</td>
</tr>
<tr>
<td>$\Sigma$ (Zemke et al [18])</td>
<td>7.766</td>
<td>145.25</td>
<td>3455</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>7.177</td>
<td>136.3</td>
<td>3362</td>
</tr>
<tr>
<td>$\Pi$ (scaled)</td>
<td>7.369</td>
<td>138.2</td>
<td>3396</td>
</tr>
</tbody>
</table>

was less than 0.5%. The rather small difference between the $\Sigma$ and $\Pi$ symmetry $C_6$ values is a consequence of the relatively small tensor polarizability.

One other set of dispersion coefficients was reported earlier by Zemke et al [18]. Their values are about 15-20% larger than the present dispersion coefficients. We cannot comment further on the accuracy of these predictions, since essentially no details were given in the publication. It is likely, however, that this calculation was performed by using oscillator strength sum rules.

C. Scaling the reduced matrix element list

The dispersion coefficients listed in Table IV could very easily underestimate the actual dispersion coefficients, since the present calculation underestimates the dipole polarizabilities compared to the large CI and coupled-cluster type calculations. Further, the oscillator strength sum rule, $\sum_i f_i$, should add up to the number of electrons. Evaluating the sum from our (valence) matrix element list yielded 6.80 instead of the expected value of 7.0.

A simple way to investigate this effect is to rescale the reduced matrix elements for the dipole transitions, so that the oscillator strengths sum to 7.0. No correction was made for the quadrupole and octupole transitions, since they only contribute to $C_8$ and $C_{10}$. The latter are less important in the interpretation of the HF ro-vibrational spectrum.

The above scaling increased the dipole polarizability to 3.583 a.u. and the tensor polarizability to 0.311 a.u. The dispersion coefficients computed from the scaled set of matrix elements are listed in Table IV. We note an overall increase in the dispersion coefficients ranging from about 3% for $C_6$ to 1% for $C_{10}$. The process of scaling reduced matrix elements
TABLE V: The dispersion coefficients for the $F_2$ ground state. Both scaled and unscaled values are given. The numbers in the square brackets denote powers of ten.

<table>
<thead>
<tr>
<th>System</th>
<th>$\gamma$</th>
<th>$C_5$ (a.u.)</th>
<th>$C_6$ (a.u.)</th>
<th>$C_8$ (a.u.)</th>
<th>$C_{10}$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unscaled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma_1$</td>
<td>$-1$</td>
<td>0.0</td>
<td>9.331</td>
<td>165.6</td>
<td>3.593[3]</td>
</tr>
<tr>
<td>$\Sigma_2$</td>
<td>$+1$</td>
<td>0.0</td>
<td>8.783</td>
<td>156.1</td>
<td>3.350[3]</td>
</tr>
<tr>
<td>$\Sigma_3$</td>
<td>$+1$</td>
<td>$-3.372$</td>
<td>8.404</td>
<td>146.8</td>
<td>3.085[3]</td>
</tr>
<tr>
<td>$\Sigma_{23}$</td>
<td>$-1$</td>
<td>0.0</td>
<td>0.844</td>
<td>15.59</td>
<td>421.9</td>
</tr>
<tr>
<td>$\Pi_1$</td>
<td>$+1$</td>
<td>2.248</td>
<td>8.373</td>
<td>149.1</td>
<td>3.157[3]</td>
</tr>
<tr>
<td>$\Pi_2$</td>
<td>$-1$</td>
<td>0.0</td>
<td>8.472</td>
<td>150.1</td>
<td>3.181[3]</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$+1$</td>
<td>$-0.562$</td>
<td>9.380</td>
<td>166.6</td>
<td>3.626[3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Scaled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma_1$</td>
<td>$-1$</td>
<td>0.0</td>
<td>9.836</td>
<td>170.0</td>
<td>3.652[3]</td>
</tr>
<tr>
<td>$\Sigma_2$</td>
<td>$+1$</td>
<td>0.0</td>
<td>9.250</td>
<td>160.3</td>
<td>3.406[3]</td>
</tr>
<tr>
<td>$\Sigma_3$</td>
<td>$+1$</td>
<td>$-3.372$</td>
<td>8.860</td>
<td>150.7</td>
<td>3.135[3]</td>
</tr>
<tr>
<td>$\Sigma_{23}$</td>
<td>$-1$</td>
<td>0.0</td>
<td>0.890</td>
<td>16.00</td>
<td>429.4</td>
</tr>
<tr>
<td>$\Pi_1$</td>
<td>$+1$</td>
<td>2.248</td>
<td>8.827</td>
<td>153.1</td>
<td>3.209[3]</td>
</tr>
<tr>
<td>$\Pi_2$</td>
<td>$-1$</td>
<td>0.0</td>
<td>8.932</td>
<td>154.1</td>
<td>3.232[3]</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$+1$</td>
<td>$-0.562$</td>
<td>9.889</td>
<td>171.1</td>
<td>3.687[3]</td>
</tr>
</tbody>
</table>

(or oscillator strengths) to conform to sum rules is a well-established practice used to help generate the underlying information needed to determine dispersion coefficients [22, 57, 60–63].

D. The $F_2$ molecule

The homonuclear $F_2$ molecule has a number of symmetries leading to the $F(2p^5)$-$F(2p^5)$ dissociation limit. There are three $\Sigma$ states, two $\Pi$ states, and one $\Delta$ state. It is convenient to introduce a parameter $\gamma$ to characterize the symmetries [41, 64]. This index is positive when the wave function stays invariant upon interchange of the magnetic quantum numbers between the two fluorine atoms. The wave function changes sign when $\gamma = -1$. 

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Since both of the dissociating species have non-zero angular momentum, there is also the possibility of a long-range quadrupole-quadrupole interaction, which leads to an asymptotic potential of \( V \sim -C_5/R^5 \). A negative sign in Table V indicates that the interaction is repulsive. The interaction constants in Table V were computed using a Hartree-Fock expectation value of the fluorine 2\( p \) orbital of \( \langle r^2 \rangle_{2p} = 1.530 \) a.u. Replacing this value of \( C_5 \) by quadrupole moments from more sophisticated calculations is simply a matter of replacing the present reduced matrix element \( \langle 2p^5 \parallel r^2 C^2 \parallel 2p^5 \rangle = -1.647 \) a.u. by a more accurate value from an alternate calculation [30, 31].

The asymptotic molecular representations for the \( \Sigma_2 \) and \( \Sigma_3 \) terms were determined by diagonalizing the quadrupole interaction (i.e., the \( C_5 \) term). However, a representation that is diagonal in \( C_5 \) is not necessarily diagonal in \( C_6 \), so there is an off-diagonal interaction connecting the \( \Sigma_2 \) and \( \Sigma_3 \) states. The actual long-range potential can be obtained by diagonalizing the 2 \( \times \) 2 interaction interaction matrix [41].

The only other estimate of the \( F_2 \) dispersion coefficients was derived from density functional theory [36]. The DFT calculation gave \( C_6 = 9.52 \) a.u. for the isotropic part of the dispersion interaction. This compares reasonably well with the values in Table V.

V. CONCLUSIONS

The box-based \( B \)-spline CI method was employed to generate lists of reduced matrix elements to describe the pseudo-excitation spectrum of fluorine. These lists were subsequently used to generate polarizabilities for the fluorine ground state, as well as dispersion coefficients characterizing the long-range part of the HF inter-atomic potential. Dispersion coefficients for the \( F_2 \) dimer were also determined.

Using the scaled list of reduced matrix elements yields oscillator strength sum rules that satisfy the Thomas-Reiche-Kuhn sum rule very well but underestimate the most advanced calculations of the fluorine polarizability by about 3-4%. This suggests a reasonable estimate of the uncertainty in the scaled HF dispersion coefficients of about \( \pm 5\% \). The uncertainty in the \( F_2 \) dispersion coefficients would be about \( \pm 10\% \), since the calculation uses the list of states twice and, therefore, the uncertainty is effectively doubled.

Prior to the present calculation, there was very little information available regarding long-range interactions involving the fluorine atom [18, 36]. We believe that the dispersion
coefficients presented here yield the best current description of the HF and F$_2$ inter-atomic interactions at large separations.

One limitation of the present work is the neglect of the spin-orbit interaction and the use of $LS$-coupling. The spin-orbit splitting for the 2p$^5$ 2P$^o$ and 2p$^4$nl levels can be as large as 0.004 hartree. A more general theory would be required if the long-range interactions between the different $J$ components were to be described to the highest precision.

VI. ACKNOWLEDGMENTS

The authors would like to thank John Coxon, Photos Hajigeorgiou, and Robert Le Roy for suggesting we undertake this work. This work was supported, in part, by the United States National Science Foundation under grants PHY-0555226 and PHY-0775575 (OZ and KB).


