PHYSICAL REVIEW A

ATOMIC, MOLECULAR, AND OPTICAL PHYSICS

THIRD SERIES, VOLUME 58, NUMBER 6 **DECEMBER 1998**

RAPID COMMUNICATIONS

The Rapid Communications section is intended for the accelerated publication of important new results. Since manuscripts submitted to this section are given priority treatment both in the editorial office and in production, authors should explain in their submittal letter why the work justifies this special handling. A Rapid Communication should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.

Radiative transitions and van der Waals coefficients for francium

M. Marinescu and D. Vrinceanu
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

H. R. Sadeghpour*
Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street,
Cambridge, Massachusetts 02138

(Received 20 August 1998)

Francium has been the least-studied alkali-metal atom until recently. We present accurate calculations for the discrete and continuum optical transitions, and dispersion coefficients for two colliding francium atoms. Spin-orbit coupling is explicitly included and the influence of core polarization on the energies and the electric dipole operator is considered. Predictions for a range of transition amplitudes that are needed for parity violation experiments are made. The van der Waals coefficients for the long-range collision of two-ground-state Fr atoms in different fine-structure levels show a departure from an established trend in other alkali-metal atoms. We comment on the differences. [S1050-2947(98)50312-5]

PACS number(s): 32.70.Cs, 32.80.Fb, 34.20.−b, 31.50.+w

Francium remains the last unexplored heavy atom with a relatively simple electronic structure. Unlike its well-studied siblings in the alkali-metal group, francium has evaded the same level of scrutiny by theory and experiment because it has no stable long-lived isotopes; for instance, ^{210}Fr has a half-life of 3.2 min. The successful trapping of ultracold alkali-metal atoms and the subsequent creation of alkali-metal Bose-Einstein condensates [1] have channeled intense attention on the spectroscopy of and collisions between alkali-metal atoms. Because of the extremely long exposure times, the ultracold environments of these traps provide magnificent laboratories for performing high-precision spectroscopy. Alkali-metal atoms are optimal for controlled experiments because (a) they have only one active electron and (b) they have experimentally favorable optical transitions. Heavier alkali-metal atoms are also of interest for tests of the standard model, the study of parity nonconservation (PNC) and nuclear anapole moment, the electric dipole moment, and the β decay [2]. Francium, as the heaviest of the alkali-metal atoms, meets this criterion.

In this Rapid Communication, we report on a detailed calculation of the optical transitions, oscillator strengths, polarizabilities, and long-range interaction energies in francium. Accurate energy levels, transition frequencies, dipole matrix elements, static and dynamic dipole polarizabilities, photoionization cross sections, fine-structure branching-ratio, and dispersion coefficients are obtained.

A considerable body of theoretical work on the structure and collisional properties of alkali metals exists [3]. Theoretical work on Fr has been scant and only a few published papers exist [4,5]. Many-body perturbation theory (MBPT) has been used in all instances to calculate a number of energy levels, transition frequencies, and dipole matrix elements. Hyperfine intervals were calculated and used to obtain nuclear magnetic moments for several isotopes of Fr.

Experimental work on Fr has been lacking mostly because francium has no stable long-lived isotope. The fast-beam experiments on the most abundant isotopic type of francium, ^{211}Fr (nuclear spin $I=5$), have yielded a series of energy levels [6]. The first optical transition measurement in Fr was the observation of the D_2 resonant line by Liberman *et al.* [7]. Recent improvements in collection efficiency in

---

*Electronic address: hsadeghpour@cfa.harvard.edu magneto-optical traps [8–10] have allowed the trapping of a significant number of Fr atoms in different isotopic types, ^{209}Fr, ^{210}Fr, ^{211}Fr, and ^{221}Fr. In some instances, the collection efficiency was increased to 56% [8]. The trapping of these short-lived isotopes provided the first opportunity for fluorescence measurements in francium.

Except for the main transition lines in Fr, i.e., the $7s_{1/2}$-$7p_{1/2}$ and $7s_{1/2}$-$7p_{3/2}$ transitions, where only recently lifetime measurements [9] and calculations [4,5] have become available, the spectroscopy of francium remains effectively unknown. No other experimental discrete oscillator strengths for various transitions in Fr are available and information on the continuum transitions does not exist. The MBPT treatment of Dzuba *et al.* [5] remains the only theoretical work which has calculated beyond the main transition lines.

The atomic structure properties of the alkali-metal atoms, other than Fr, have been used to calculate the dynamic response of the atoms to electromagnetic radiation and predict the strength of the interaction between colliding atoms [11,12]. These van der Waals coefficients have been utilized to calculate collisional properties of cold alkali-metal atoms [3]. A variety of theoretical techniques have been employed, but an accurate and straightforward scheme has been to use a one-electron potential for the motion of the valence electron in the average field of the core electrons. This recognition is based on the fact that the Rydberg electron moves outside a closed core and participates in the interaction with other atoms.

The starting point for the calculations reported here is the construction of a local, angular momentum-dependent parametric potential that describes accurately the interaction of the valence electron with the core electrons [11]. As with other alkali-metal atoms, we anticipate that a one-active electron potential will provide sufficient accuracy in predicting the spectroscopic features of Fr.

The form this one-active electron potential takes is

$$V_l^{(j)}(r)=\frac{Z_{lj}(r)}{r}-\frac{\alpha_c}{2r^4}[1-e^{-(r/r_c^{(j)})^6}], \qquad (1)$$

where α_c is the static dipole polarizability of the Fr$^+$ ionic core and the effective radial charge $Z_{lj}(r)$ is given by

$$Z_{lj}(r)=1+(z-1)e^{-a_1^{(j)}r}+r(a_3^{(j)}+a_4^{(j)}r)e^{-a_2^{(j)}r}. \qquad (2)$$

In Eq. (2), z is the charge on the nucleus, $z=87$, and $r_c^{(j)}$ is a cut-off radius that truncates the short-range contribution of the polarization potential. The parameters of this potential are chosen to be j and l dependent. These parameters are obtained by requiring that the energy eigenvalues of the one-electron Hamiltonian reproduce the observed energy levels in Fr [6–10]. The fine-structure splitting for the $7p_{1/2}$ and $7p_{3/2}$ is 1687 cm^{-1}, about 9% of the binding energy. Similarly large fine-structure splittings exist for the d levels. We have henceforth chosen to construct two potentials, one for each $j_+=l+1/2$ and $j_-=l-1/2$ levels. This construction is meaningful for francium, in contrast with previous l-dependent potentials [11] for other alkali metals, in that the spin-orbit coupling is explicitly included.

TABLE I. Radial matrix elements for discrete excitations in Fr.

$nlj-n'l'j'$	$\langle n'l'j'\|r\|nlj\rangle$			
	Present	Ref. [5]	Ref. [4]	Ref. [9]
$7s_{1/2}$-$7p_{1/2}$	−5.2382	−5.271	5.1779	5.238
$7s_{1/2}$-$7p_{3/2}$	−5.1082	−5.133	5.0148	5.108
$7s_{1/2}$-$8p_{1/2}$	−0.3721	−0.3684		
$7s_{1/2}$-$8p_{3/2}$	−0.7865	−0.8004		
$7s_{1/2}$-$9p_{1/2}$	−0.1172			
$7s_{1/2}$-$9p_{3/2}$	−0.3636			
$8s_{1/2}$-$7p_{1/2}$	5.1813	5.167	5.1387	
$8s_{1/2}$-$7p_{3/2}$	6.4511	6.469	6.4708	
$8s_{1/2}$-$8p_{1/2}$	−12.3270	−12.25		
$8s_{1/2}$-$8p_{3/2}$	−11.5375	−11.48		
$8s_{1/2}$-$9p_{1/2}$	−1.1969			
$8s_{1/2}$-$9p_{3/2}$	−1.9363			
$9s_{1/2}$-$7p_{1/2}$	1.2368			
$9s_{1/2}$-$7p_{3/2}$	1.1948			
$9s_{1/2}$-$8p_{1/2}$	11.4410			
$9s_{1/2}$-$8p_{3/2}$	13.7877			
$9s_{1/2}$-$9p_{1/2}$	−21.3834			
$9s_{1/2}$-$9p_{3/2}$	−19.6850			

A particularly appealing aspect of this potential is the inclusion of the core interaction term, which arises due to the electric field of the valence electron. Core polarization effects are greatly enhanced for heavier systems. Optical double resonance measurements of Arnold *et al.* [6] indicate a large core polarization effect. Indeed, we trust our calculation to provide accurate dynamical information on the interaction of the valence electron with the core.

Furthermore, we take the valence electron to move adiabatically in the field of the core. The core perturbation also manifests itself as a correction to the electric dipole operator

$$\mathbf{r}\to\mathbf{r}\left(1-\frac{\alpha_c}{r^3}(1-e^{-(r/r_c)^3})\right). \qquad (3)$$

The effect of the core polarization is to distort the dipole operator and modify the magnitude of the radial matrix element.

Table I lists a few selected radial dipole matrix elements. They are compared with available experimentally determined values and sophisticated MBPT calculations. These transitions are important for PNC tests, because a PNC signal in Fr is mediated by the Z bosons, which induce a small electric dipole-allowed component in the PNC transition, $7s_{1/2}-8s_{1/2}$. The discrepancy between our results and the calculated radial matrix elements of Ref. [5] is less than 0.7%, except for the $7s$-$8p_{3/2}$ transition where the difference is 1.7%. Differences with the calculations of Ref. [4] are as large as 4% for the dominant $7s_{1/2}$-$7p_{3/2}$ transition. An experimental determination of the $8p_{1/2,3/2}$ lifetimes should assist in resolving these discrepancies. A comprehensive listing of energy levels, transition frequencies, matrix elements, and polarizabilities will be provided elsewhere [13].

Here, we briefly comment that the photoionization cross section for ejecting photoelectrons in the $j_+ = 3/2$ angular-momentum state contains a Cooper zero near 3.5 eV, above the first ionization threshold. The cross section in the $j_- = 1/2$ channel, on the other hand, peaks near 2.5 eV and at its peak has a value more than three times that of the Cs photoionization cross section.

A measure of the spin-orbit coupling is the atomic line-strength ratio. This ratio of the transition strength to j_- and j_+ levels is given by $R = \mathcal{S}_{j_-} / \mathcal{S}_{j_+}$, where $\mathcal{S}_{j'} = |\langle n'j' || r^{(1)} || nj \rangle|^2$. [The reduced matrix element $\langle n'j' || r^{(1)} || nj \rangle$ is related to the usual radial matrix element, for an initial s state, as $\langle n'l'j' | r | nlj \rangle = \sqrt{3/(2j'+1)} \langle n'j' || r^{(1)} || nj \rangle$.] We calculate $R = \mathcal{S}_{1/2} / \mathcal{S}_{3/2}$ for the main transitions in Fr to be 0.525. The observed value for R is 0.526(3) [9]. In the absence of the spin-orbit coupling, R will simply be a statistical ratio of $2/4 = 0.5$. Departure from this mean value speaks to the strength of the spin-orbit coupling in Fr.

For collisions between two ground-state alkali-metal atoms, the long-range dimer potential is of the form

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \tag{4}$$

where C_n for $n = 6,8,10$ are the dispersion coefficients. The expressions for C_n can be formulated in terms of integrals over atomic multipole polarizabilities at imaginary frequencies [14].

We build molecular wave functions in different symmetries from the atomic wave functions

$$|nljm\rangle = \sum_{m_l, m_s} \langle lm_l, sm_s | jm \rangle | nlm_l j \rangle \chi_{m_s}, \tag{5}$$

where all the symbols have their usual meanings and χ_{m_s} stands for the spin wave function.

In general, the total wave functions for two noninteracting atoms in arbitrary $|n_1 l_1 j_1 m_1\rangle$ and $|n_2 l_2 j_2 m_2\rangle$ states are given by

$$\begin{aligned} &|n_1 n_2, (l_1 \tfrac{1}{2}) j_1, (l_2 \tfrac{1}{2}) j_2, JM\rangle \\ &\quad = \sum_{m_{j_1}, m_{j_2}} \langle j_1 m_1, j_2 m_2 | JM \rangle | n_1 l_1 j_1 m_1 \rangle | n_2 l_2 j_2 m_2 \rangle. \end{aligned} \tag{6}$$

Then, the two ground-state atom wave functions in the infinite separation limit are written as

$$|n_g n_g, (0\tfrac{1}{2})\tfrac{1}{2}, (0\tfrac{1}{2})\tfrac{1}{2}, JM\rangle \equiv |n_g n_g JM\rangle. \tag{7}$$

The molecular symmetries associated with these ground states are the ${}^1 0_g^+$, ${}^3 0_u^+$, and ${}^3 1_u$ symmetries whose asymptotic wave functions are denoted, respectively, by $|n_g n_g 00\rangle$, $|n_g n_g 10\rangle$, and $|n_g n_g 1 \pm 1\rangle$.

The C_6 dispersion coefficients for each molecular symmetry are the following:

TABLE II. Dispersion coefficients for two-ground state francium atoms.

Molecular symmetry	C_6	$C_8 \times 10^{-5}$	$C_{10} \times 10^{-8}$
${}^1 0_g^+$	3929.27	6.647 75	1.069 90
${}^3 0_u^-$	3947.25	6.647 69	1.069 90
${}^3 1_u$	3933.76	6.647 73	1.069 90

For the ${}^1 0_g^+$ symmetry,

$$C_6 = \frac{2}{9} (2 S_{13}^{11} + S_{33}^{11}). \tag{8}$$

For the ${}^3 0_u^+$ symmetry,

$$C_6 = \frac{2}{81} (8 S_{11}^{11} + 2 S_{13}^{11} + 17 S_{33}^{11}). \tag{9}$$

For the ${}^3 1_u$ symmetry,

$$C_6 = \frac{2}{81} (2 S_{11}^{11} + 14 S_{13}^{11} + 11 S_{33}^{11}). \tag{10}$$

Similar expressions exist for C_8 and C_{10} van der Waals coefficients [13]. The infinite sums over the intermediate states

$$S_{pq}^{lL} = \sum_{n_1, n_2} \frac{(n_g 0 \tfrac{1}{2} | r^l | n_1 l \tfrac{p}{2})^2 (n_g 0 \tfrac{1}{2} | r^L | n_2 L \tfrac{q}{2})^2}{E_{n_1 l \frac{1}{2}} + E_{n_2 L \frac{q}{2}} - 2 E_{n_g 0 \frac{1}{2}}} \tag{11}$$

are calculated using a generalized version of the Dalgarno-Lewis method [11,12,14], by transforming the infinite sums into a set of coupled inhomogeneous differential equations, which in turn are solved using algorithms developed in Ref. [11]. Altogether, 14 such sums will have to be evaluated. If the spin-orbit coupling is neglected, the expressions for C_6 reduce to just one term, $C_6 = \frac{2}{3} S_{13}^{11}$.

The values for the dispersion coefficients for the long-range interaction between two ground-state Fr atoms are presented in Table II. To our knowledge, these are the first values of the long-range coefficients for francium in the literature. For comparison, the C_6 value for cesium was calculated to be 6331 and the same value for Rb was 4426 [11]. Francium dispersion coefficients deviate from the established trend in other alkali-metal atoms in that the van der Waals coefficients increase with increasing atomic number. The source of this departure lies with the first ionization potential in Fr, 32 849 cm^{-1} [6], which is larger than similar binding energies for Rb and Cs [15]. The monotonic lowering of the binding energy in alkali-metal atoms is arrested with francium. The primary effect of this increase in binding energy will be a decrease of the magnitude of the dominant terms in Eq. (11) and hence a general lowering of the van der Waals coefficients.

The experimental advances of the last few years, laser cooling in particular, have made the spectroscopy of francium a reality. As the heaviest alkali metal, francium is ideally suited for precision measurements and calculations. The availability of ground electronic potential-energy curves for

Fr_2 in the small and intermediate internuclear ranges, when combined with the long-range dimer potentials of this work can address the feasibility of creating a francium dilute condensate.

This work was supported partially by the Office of Naval Research and by the National Science Foundation through a grant to the Institute for Theoretical Atomic and Molecular Physics at the Harvard-Smithsonian Center for Astrophysics.

[1] C. J. Myatt, E. A. Burt, R. W. Ghrist, E. A. Cornell, and C. E. Wieman, Phys. Rev. Lett. **78**, 586 (1997); M. R. Andrews *et al.*, Science **275**, 637 (1997).

[2] J. A. Behr *et al.*, Hyperfine Interact. **81**, 197 (1993); Z.-T. Lu *et al.*, Phys. Rev. Lett. **72**, 3791 (1994); C. S. Wood *et al.*, Science **275**, 1759 (1997).

[3] R. Cote and A. Dalgarno, Phys. Rev. A **50**, 4827 (1994); E. Tiesinga, B. J. Verhaar, and H. T. C. Stoof, *ibid.* **47**, 4114 (1993); P. A. Ruprecht *et al.*, *ibid.* **51**, 4704 (1995); J. P. Burke, J. L. Bohn, B. D. Esry, and C. H. Greene, Phys. Rev. Lett. **80**, 2097 (1998); P. S. Julienne, F. H. Mies, E. Tiesinga, and C. J. Williams, *ibid.* **78**, 1880 (1997); H. Wang and W. C. Stwalley, J. Chem. Phys. **108**, 5767 (1998).

[4] W. R. Johnson, Z. W. Liu, and J. Sapristein, At. Data Nucl. Data Tables **64**, 279 (1996); J. Sapristein, Rev. Mod. Phys. **70**, 55 (1998).

[5] V. A. Dzuba, V. V. Flambaum, and O. P. Shushkov, J. Phys. B **17**, 1953 (1984); V. A. Dzuba, V. V. Flambaum, and O. P. Shushkov, Phys. Rev. A **51**, 3454 (1995).

[6] E. Arnold *et al.*, J. Phys. B **22**, L391 (1989); **25**, 3511 (1990); J. Bauche *et al.*, *ibid.* **19**, L593 (1986); H. T. Duong *et al.*, Europhys. Lett. **3**, 175 (1987); S. V. Andreev, V. S. Letokhov, and V. I. Mishin, Phys. Rev. Lett. **59**, 1274 (1987); J. Opt. Soc. Am. B **5**, 2190 (1988).

[7] S. Liberman *et al.*, C. R. Acad. Sci., Ser. II: Mec. Phys., Chim., Sci. Terre Univers **268**, 253 (1987).

[8] Z.-T. Lu *et al.*, Phys. Rev. Lett. **79**, 994 (1997).

[9] J. E. Simsarian *et al.*, Phys. Rev. A **57**, 2448 (1998); W. Z. Zhao *et al.*, Phys. Rev. Lett. **78**, 4169 (1997).

[10] J. E. Simsarian *et al.*, Opt. Lett. **21**, 1939 (1996); J. E. Simsarian, W. Z. Zhao, L. A. Orozco, and G. D. Sprouse, Phys. Rev. A (to be published).

[11] M. Marinescu, R. H. Sadeghpour, and A. Dalgarno, Phys. Rev. A **49**, 982 (1994), and references therein.

[12] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995).

[13] M. Marinescu and H. R. Sadeghpour (unpublished).

[14] A. Dalgarno and W. D. Davison, Adv. At. Mol. Phys. **2**, 1 (1966).

[15] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl Bur Stand. (U.S) (U.S. GPO, Washington, DC, 1971), Vol. I-III.