# Bounds to the lifetime of the Ar XVII $2\,^3S$ state*

M. T. Anderson and F. Weinhold†
*Department of Chemistry, Stanford University, Stanford, California 94305*
(Received 15 October 1974)

Bounds to the emission probability and lifetime are calculated for the Ar XVII $2\,^3S$ state using Drake's form of the magnetic dipole transition operator. Variational wave functions of increasing quality lead to theoretical error bounds of about 0.24%, thereby sharpening the discrepancy between theoretically and experimentally determined lifetimes.

## I. INTRODUCTION

Gabriel and Jordan[1] first identified a sequence of lines in the solar x-ray spectrum as originating from the $2\,^3S$ state of the heliumlike ions. They postulated that the decay mechanism occurs via the forbidden magnetic dipole transition, $2\,^3S \rightarrow 1\,^1S$, rather than by the two-photon electric dipole emission as had been previously supposed.[2] Since the transition probability can be used to predict excitation rate ratios, electron densities, and (ultimately) elemental abundances in stellar atmospheres,[3] this identification stimulated further theoretical and experimental investigations of the lifetimes of these metastable states.

Schmieder and Marrus,[4] using beam foil spectroscopy, soon reported the first laboratory measurement of the lifetime of the $2\,^3S$ state of ArXVII, and lifetimes have subsequently been measured for HeI,[5] ClXVI,[6] TiXXI,[7] VXXII, and FeXXV.[8] Complementing the laboratory experiments were theoretical calculations by Drake[9] of the emission probabilities for He and the He-like ions through FeXXV. A more recent calculation[10] has included terms of higher order in $\alpha Z$ ($\alpha$ = the fine structure constant, $Z$ = the nuclear charge) and may be even more accurate for the heavier heliumlike ions. A comparison of these theoretical calculations with the experimental observations reveals an obvious discrepancy for the lifetimes of ArXVII and other of the heavy ions for which the experimental values are as much as 25% lower than the theoretical ones.

In this paper we examine the ArXVII $2\,^3S \rightarrow 1\,^1S$ magnetic dipole transition by the method of upper and lower bounds.[11] This method was recently applied to a series of allowed electric dipole transitions in the helium[12] and beryllium[13] sequences; the present work serves as the first application of the method to forbidden transitions. In view of the discrepancy between experimental and theoretical results, we examine in particular the theoretical error which can result from the inadequacy of the nonrelativistic wave functions for calculating the magnetic dipole moment. It is well known that wave functions of presumably high quality based on an energy-optimization criterion may be quite inadequate to describe effects which derive large contributions from less energy-important areas of configuration space.[14] Since little information is available to show how the magnetic dipole operator "weights" various details of the wave functions, the present calculation was undertaken to assess possible errors arising from the use of such inexact solutions of the nonrelativistic problem.

Using Drake's form of the magnetic dipole operator, we calculate bounds to the emission probability and lifetime of the ArXVII $2\,^3S$ state using a series of highly correlated variational wave functions of increasing quality. Our calculations show that the theoretical uncertainties are but a fraction of 1% of the calculated lifetimes. Since the magnetic dipole operator derived by Drake neglects only terms of rather minor importance (less than "1 or 2%"),[9] the calculation suggests the high reliability of the theoretical lifetimes, and seems to confirm that the experimental results are in substantial conflict with the theoretical understanding of such transitions.

## II. BOUNDS TO THE MAGNETIC DIPOLE MOMENT

The equations previously derived for bounds to transition moments[11] remain formally valid for the case of magnetic dipole transitions, provided the appropriate operator is employed. These equations bound the transition matrix element $w_{ab}$,

$$w_{ab} = \langle \Psi_a | W | \Psi_b \rangle, \tag{1}$$

where $\Psi_a$ and $\Psi_b$ are the exact nonrelativistic wave functions for the initial and final states, and $W$ is the equivalent nonrelativistic magnetic dipole transition operator correct to terms of relative order $\alpha^2 Z^2$. For the $2\,^3S_1 \rightarrow 1\,^1S_0$ transition, the $\alpha^2 Z^2$ correction is the first nonvanishing term. We use the form derived by Drake,[9]

TABLE I. Nonlinear parameters $\xi$, $\eta$, and "overlap error" $\epsilon$ for each of the final wave functions.

| State | No. of terms | $\xi$ | $\eta$ | $\epsilon\,(10^{-4})$ |
|---|---|---|---|---|
| | 10 | 19.0 | 19.0 | 16.6 |
| | 20 | 20.5 | 20.5 | 4.26 |
| $1\,^1S$ | 30 | 21.2 | 21.2 | 2.13 |
| | 40 | 21.9 | 21.9 | 1.11 |
| | 49 | 22.5 | 22.5 | 0.93 |
| | 10 | 8.64 | 18.0 | 16.5 |
| | 20 | 9.72 | 18.0 | 3.85 |
| $2\,^3S$ | 30 | 10.08 | 18.0 | 1.76 |
| | 40 | 10.62 | 18.0 | 0.72 |
| | 49 | 10.8 | 18.0 | 0.62 |

$$W=\mu_B\Big[-\frac{2}{3m^2c^2}(p_1^2-p_2^2)-\frac{1}{6}\Big(\frac{\omega}{c}\Big)^2(r_1^2-r_2^2)+\frac{Ze^2}{3mc^2}\Big(\frac{1}{r_1}-\frac{1}{r_2}\Big)\Big], \tag{2}$$

where $\mu_B=e\hbar/2mc$ (the Bohr magneton), and $\omega$ is the transition frequency. The operator (2) contains both finite wavelength and relativistic energy corrections to the magnetic dipole operator. In common with the usual nonrelativistic theory of allowed transitions, the next relativistic correction to (1) and (2) is of order $\alpha^2Z^2$ relative to the first nonvanishing term.

The calculations use the approximate nonrelativistic wave functions $\Phi_a$ and $\Phi_b$ and the approximate transition moment $\tilde{w}_{ab}$,

$$\tilde{w}_{ab}=\langle\Phi_a|W|\Phi_b\rangle\,. \tag{3}$$

While bounds evaluated with (3) render a rigorous account of the theoretical error which results from using approximations to the exact nonrelativistic wave functions, they do not give rigorous bounds to the true transition moments to the extent that further relativistic corrections to the wave functions and transition operator of relative order $\alpha^2Z^2$ and higher are not accounted for. When the magnetic dipole operator is expressed in atomic units, $\hbar=m=e=1$, bounds to the averaged emission probability $A$ are obtained from the transition moment bounds by

$$A^{\pm}(2\,^3S\to 1\,^1S)=\frac{4}{3}\Big(\frac{\Delta E}{c}\Big)^3|w_{ab}^{\pm}|^2\times 2.1489\times10^{-17}\ \text{sec}^{-1}, \tag{4}$$

where $\Delta E$ is the difference in the true energies $E_b$ and $E_a$. The bounds to the lifetime $\tau$ are simply

$$\tau_{2\,^3S}^{\pm}=1/A^{\pm}\,. \tag{5}$$

The argon XVII wave functions used to calculate the lifetimes were variational solutions of the Schrödinger wave equation $H\Psi=E\Psi$, where $H$ is the spin-independent, nonrelativistic Hamiltonian,

$$\mathcal{H}=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{18}{r_1}-\frac{18}{r_2}+\frac{1}{r_{12}}\,. \tag{6}$$

The trial wave functions,

$$\Phi=\sum_K C_K\chi_K\,, \tag{7}$$

consisted of linear combinations of Hylleraas-type basis functions $\chi_K$ containing positive, integral powers of $r_1$, $r_2$, and $r_{12}$,

$$\chi_K(1,2)=(1\pm P_{12})r_1^i r_2^j r_{12}^k\exp(-\xi r_1-\eta r_2)\,. \tag{8}$$

In (8), $P_{12}$ is the permutation operator, and the plus or minus sign applies for the $1\,^1S$ state or the $2\,^3S$ state, respectively. Wave functions consisting of 10, 20, 30, 40, and 49 terms were calculated in order to reveal the variation in the uncertainty of the calculated $2\,^3S$ lifetimes with the wave-function quality. The full calculation using 49 singlet and 49 triplet basis functions corresponds to the set of basis functions with $(i+j+k)\leq 6$, $i\geq j$, and $k\leq 5$. The nonlinear parameters $\xi$ and $\eta$ were moderately optimized with the constraints $\xi=\eta$ for the singlet state and $\eta=Z=18$ for the triplet state. The parameter $\epsilon$, the "overlap error,"

$$\epsilon=(1-S_-^2)^{1/2} \tag{9}$$

where $S_-$ is a lower bound to the overlap between the true and approximate wave functions, is a convenient measure of the quality of these wave functions. Table I contains the comparison of overlap errors for each of the wave functions and also lists the final values of the nonlinear parameters $\xi$ and $\eta$. Lower bounds to overlap for these functions were calculated in the usual manner[12] from Weinberger's formula.[15] The true energies required by the overlap formulas were taken from the extensive variation-perturbation calculations of Midtal and co-workers.[16]

A rigorous application of the bounds equations also requires the quantity $\langle\Psi_a|W^2|\Psi_a\rangle$ or its upper bound. We approximate this quantity by the expectation value, $\langle\Phi_a|W^2|\Phi_a\rangle$, where $\Phi_a$ is the 49-term variational $1\,^1S$ function. This substitution is well justified in that (i) the 49-term wave function is of extremely high accuracy, as can be seen in Table I, (ii) expectation values tend to be calculated much more reliably than transition moments, (iii) the calculation is rather insensitive to the exact value of $\langle\Psi_a|W^2|\Psi_a\rangle$, and (iv) the values of $\langle\Phi_a|W^2|\Phi_a\rangle$ calculated by either 10-term or 49-term wave functions are in close agreement, in-

TABLE II. Upper and lower bounds to the emission coefficient $A$ and lifetime $\tau$ for the magnetic dipole transition Ar XVII $2\,^3S \rightarrow 1\,^1S$.

| No. of terms | $A$ ($10^6$ sec$^{-1}$) | $\tau$ (nsec) | % error |
|---|---|---|---|
| 10 | 4.718 ± 0.216 | 212.4 ± 9.7 | 4.58 |
| 20 | 4.708 ± 0.053 | 212.4 ± 2.4 | 1.13 |
| 30 | 4.709 ± 0.026 | 212.4 ± 1.2 | 0.57 |
| 40 | 4.708 ± 0.012 | 212.4 ± 0.6 | 0.26 |
| 49 | 4.708 ± 0.011 | 212.4 ± 0.5 | 0.24 |

dicating that the expectation value converges quite quickly. Thus, no significant loss of rigor results from this substitution in the present case.

The calculated upper and lower bounds to the emission probabilities and lifetimes for the ArXVII $2\,^3S \rightarrow 1\,^1S$ transition (using successively 10-, 20-, 30-, 40-, and 49-term wave functions for each state) are shown in Table II. These same results are depicted graphically in Fig. 1, where we have superimposed the most precise experimental determination (Ref. 7). In Table II, the $A$ and $\tau$ values are presented in the form

mean value ± error,

where "mean value" is the average of the upper and lower bounds and "error" is half their difference. The mean of the upper and lower bounds is in each case highly accurate; the uncertainty is already less than 5% for the 10-term calculation, and quickly decreases to well below 1% beyond 20 terms. The final theoretical uncertainty is about one quarter of 1% in the 49-term calculation.

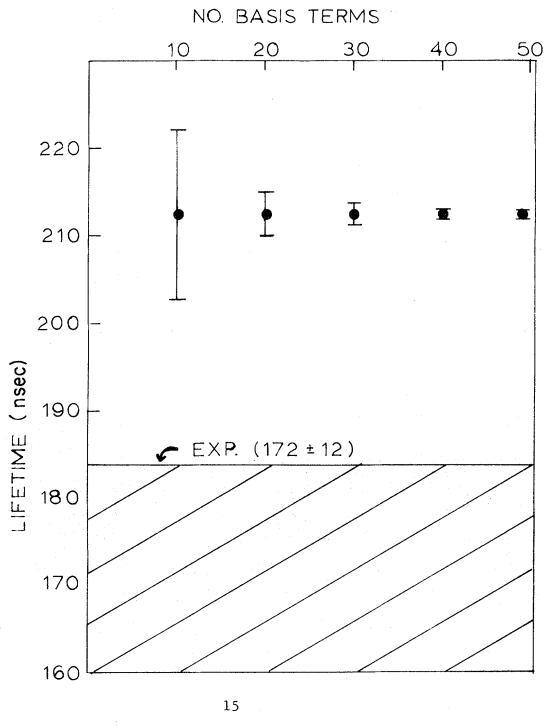


FIG. 1. Bounds to the lifetime of the Ar XVII $2\,^3S$ state for various expansion lengths of the wave functions. The experimental value is also shown (Ref. 7 of text).

TABLE III. Comparison of theoretical and experimental determinations of the lifetime of the $2\,^3S$ state of Ar XVII.

| Investigator | $\tau$ (nsec) |
|---|---|
| Drake | 212.4[a] |
| Schwartz | 208[b] |
| Beĭgman and Safronova | 196[c] |
| Feneuille and Koenig | 215[d] |
| Johnson and Lin | 208.0[e] |
| Present authors | 212.4 ± 0.5 |
| Schmieder and Marrus | 172 ± 30[f] |
| Gould, Marrus, and Schmieder | 172 ± 12[g] |

[a] See Ref. 9. The value listed in Ref. 9 is actually 212.7, but inversion of the listed emission probability gives the value shown above.

[b] Private communication cited by R. Marrus and R. W. Schmieder, Phys. Rev. A 5, 1160 (1972).

[c] I. L. Beĭgman and U. I. Safranova, Zh. Eksp. Teor. Fiz. 60, 2045 (1971) [Sov. Phys.-JETP 33, 1102 (1971)].

[d] S. Feneuille and E. Koenig, C. Acad. Sci. B 274, 46 (1972).

[e] See Ref. 10.

[f] See Ref. 4.

[g] See Ref. 7.

Even the calculation using 10-term wave functions strongly confirms the disparity between theoretical and experimental lifetimes. In Table III we list the reported theoretical and experimental results. The 49-term variational calculation of the present work should correspond most closely to the perturbation calculation by Drake, except that the present wave functions are somewhat better due to the variational selection of nonlinear parameters. The Beĭgman and Safranova calculation, which had agreed most closely with the experimental lifetimes, is far outside the theoretical bounds of the present work.

In conclusion, we have shown that the theoretical error associated with the use of approximate nonrelativistic wave functions can be made extremely small, and that this error does not account for the discrepancy between the theoretical and experimental lifetimes for the ArXVII $2\,^3S$ state. Ruling out this source of error in the theoretical calculations reinforces the conclusion that either the experimental results are subject to some as yet un-

identified systematic error, or that an alternative mechanism is responsible for depopulating the $2^3S$ metastable state.

*Note added in manuscript.* After this work was completed, an abstract came to our attention which indicates that observations conducted over longer flight paths will result in higher values for the experimental lifetimes.[17]

---

*Supported in part by NSF Grant No. GP-6112A1.

†Camille and Henry Dreyfus Foundation Fellow.

[1]A. H. Gabriel and C. Jordan, Nature 221, 947 (1969).

[2]G. Breit and E. Teller, Astrophys. J. 91, 215 (1940).

[3]A. H. Gabriel and C. Jordan, Mon. Not. R. Astron. Soc. 145, 241 (1969).

[4]R. W. Schmieder and R. Marrus, Phys. Rev. Lett. 25, 1245 (1970); a more precise value for the lifetime is given in Ref. 7.

[5]H. W. Moos and J. R. Woodworth, Phys. Rev. Lett. 30, 775 (1973).

[6]C. L. Cocke, B. Curnette, J. R. Macdonald, and R. Randall, Phys. Rev. A 9, 57 (1974).

[7]H. Gould, R. Marrus, and R. W. Schmieder, Phys. Rev. Lett. 31, 504 (1973).

[8]H. Gould, R. Marrus, and P. J. Mohr, Phys. Rev. Lett. 33, 676 (1974).

[9]G. W. F. Drake, Phys. A 3, 908 (1971). Also see the following: G. Feinberg and J. Sucher, Phys. Rev. Lett. 26, 681 (1971); G. W. F. Drake, Phys. Rev. A 5, 1979 (1972); Phys. Rev. A 9, 2799 (1974). We thank an anonymous referee for his clarifying remarks concerning the magnetic dipole operator.

[10]W. R. Johnson and C.-P. Lin, Phys. Rev. A 9, 1486 (1974).

[11]F. Weinhold, Phys. Rev. Lett. 25, 907 (1970); J. Chem. Phys. 54, 1874 (1971).

[12]M. T. Anderson and F. Weinhold, Phys. Rev. A 9, 118 (1974); Phys. Rev. A 10, 1457 (1974).

[13]J. S. Sims and R. C. Whitten, Phys. Rev. A 8, 2220 (1973).

[14]S. Chandrasekhar, Astrophys. J. 100, 176 (1944); S. Ehrensen and P. E. Phillipson, J. Chem. Phys. 34, 1224 (1961).

[15]H. F. Weinberger, J. Res. Natl. Bur. Stand. (U.S.) B 64, 217 (1960).

[16]J. Midtal, Phys. Rev. 138, A1010 (1965); K. Aashamar, G. Lyslo, and J. Midtal, J. Chem. Phys. 52, 3324 (1970); G. Lyslo, K. Aashamar, and J. Midtal, Int. J. Quantum Chem. 5, 583 (1971); K. Aashamar, J. Midtal, and G. Lyslo, J. Chem. Phys. 60, 3403 (1974).

[17]C. L. Cocke, J. A. Bednar, B. Curmutte, and R. Randall, in Fourth International Conference on Atomic Physics, Abstracts of Contributed Papers, Heidelburg, 1974 (unpublished), p. 187.