

# Magnetic Quadrupole Lifetimes of $np^5(n+1)s$ $J = 2$

## States of Rare Gases

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Relativistic configuration-interaction calculations yield lifetimes of 19.8, 32.2, 35.0, 48.2, and 84.9 s for Ne, Ar, Kr, Xe, and Rn. For Ar, Kr, and Xe the experimental values are 38, 39, 43 s. This resolves the theoretical-experimental discrepancy, where theory could be as large as twice experiment (Xe). An accurate description of the  $p^5d$  basis function is essential.

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## I. INTRODUCTION AND METHODOLOGY

In the mid 1990's the first metastable lifetimes  $> 1$  s were measured [1,2] for Ar, Kr, and Xe using a magneto-optical trap. For isotopes with zero spin ( $I = 0$ ), decays are magnetic quadrupole in nature, with lifetimes of  $\sim 40$  s. Multi-configurational Dirac-Fock calculations [2] yielded lifetimes of 51, 63, and 96 s for atoms respectively. These are large discrepancies, which increase with  $Z$ , even though the energy differences are accurate to 1% [2]. It is of considerable interest to discover what the difficulty is.

In carrying out calculations with a relatively unknown operator (M2) it is useful to know what the matrix element selection rules are, and the  $r$  dependence of the radial integrand. The former are available in Grant's work [3], where it is found that one electron integrals have opposite parity spinors,  $|j - 2| \leq j' \leq j + 2$ , and for this transition  $\kappa\kappa' > 0$ . From an angular standpoint then, the selection rules for this transition are the same as the more familiar electric dipole ones. Illustrations are  $(s_{1/2}, p_{1/2}, p_{3/2}, d_{3/2}, d_{5/2}) \rightarrow (p_{3/2}, d_{3/2}, s_{1/2} + d_{5/2}, p_{1/2} + f_{5/2}, p_{3/2} + f_{7/2})$ .

The radial integrand, however, is proportional to  $r^2$  for M2 and not  $r$  (length gauge) as for E1 transitions in the cases of optical or near-optical transitions. This places greater emphasis on constructing accurate radial functions for larger values of  $r$  than for E1 transitions. In the spirit of the First Order Theory of Oscillator Strengths (FOTOS) [4], accurate radial functions for the  $np^5(n+1)s$  and  $np^5nd$  configurations in the upper state, and the  $np^5(n+1)p$  configuration in the lower state should be particularly important. This especially proves to be the case for the  $p^5d$  configuration. Not only must the description of the  $d$  radial function be accurate, but so must the coefficient of this basis function. This means that whatever large correlation effects are present for  $p^5s$  (the reference configuration), the analogous effects must be present for  $p^5d$ . These effects are frequently second order in nature, i.e. triple excitations with respect to  $p^5s$ . Their inclusion preserves the proper energy difference between the  $p^5s$  and  $p^5d$  basis functions.

Our relativistic configuration-interaction (RCI) reference functions, here  $p^6$  and  $p^5s$ , are

built up from determinantal functions whose one electron radial functions are obtained from a Dirac-Fock calculation, using Desclaux's program [5]. The Dirac-Coulomb Hamiltonian is used; during the RCI stage, the Dirac-Breit Hamiltonian may be employed. Correlation configurations are created by exciting one or two subshells in the reference configuration. Wavefunctions for each configuration are made eigenstates of  $J^2$ ,  $J_z$ , and parity. Radial functions for the unoccupied subshells are represented by relativistic screened hydrogenic functions, whose effective charge  $Z^*$  is determined during the energy variational process, i.e. diagonalization. Choosing  $Z^*$  to match the  $\langle r \rangle$  of the excited subshell produces an excellent starting point of the iteration process.

The  $J = 0$  and  $J = 2$  states are calculated with separate radial bases, and thus are not orthogonal. Non-orthogonality effects can be substantial ( $\sim 20\%$ ) in neutral and lightly ionized species [6]. We have been treating these since 1969 [7] using the method of King *et al* [8] which is based on the corresponding orbital method of Amos and Hall [9]. Initially, calculation times were rather slow, but starting in 1978 [10–13] an extensive use of symmetry enabled speed gains of up to a factor of 1000 to be achieved. Very recently, an equivalent methodology has been developed, called the relaxed orbital method [14], which is based on Löwdin cofactors [15].

## II. RESULTS

Our results apply to the nuclear spinless isotopes, as lifetimes of isotopes with spin can be considerably shorter due to the mixing of nearby fine structure levels by the hyperfine Hamiltonian [2].

Our first and most careful calculation was for Xe, as this exhibits the largest discrepancy. For the  $J = 2$  state a 3 configuration calculation with  $5p^5(6s + 7s + 5d)$  determines a good representation for the  $7s$  and  $5d$  radials. The other radials are frozen, having been previously determined by a separate Dirac-Fock calculation on  $5p^56s$ . This yields an energy difference of  $14\,465\text{ cm}^{-1}$  between  $5p^56s$  and the lowest  $5p^55d$   $J = 2$  level in good agreement with the experimental value [16] of  $13\,255\text{ cm}^{-1}$ . This gives us confidence that the diffuse nature of the  $5d$  and  $7s$  radials are properly accounted for. We next correlate the  $J = 2$  state using the following single and double subshell excitations:  $6s \rightarrow vs + vd + vg$ ;  $5p6s \rightarrow vsvp + vpv d + vdvf + vfv g$ ;  $5p \rightarrow vp + vf$ ;  $5p^2 \rightarrow vs^2 + vp^2(T) + vd^2(T) + vf^2(T) + vg^2(T) + vsvd + vpvf$ ;  $5s5p \rightarrow vsvp(T) + vpv d(T) + vdvf(T) + vfv g(T)$ ;  $5s6s \rightarrow vp(5p + vp)$ ;  $4d6s \rightarrow 5pvp + 5pvf$ . The  $vl$  are correlation radials (virtuals) which are quite different (much more compact) than the  $5d$  and  $7s$ . The  $4d$  excitations chosen are those which FOTOS [4] suggests may be important.

Equivalent excitations are included for the  $J = 0$  wavefunction. At this stage the lifetime is  $64.2\text{ s}$  – a distinct improvement, but still well off experiment. The calculation was also done in three layers – opening  $5p$ , then  $5s$ , then  $4d$ . Opening up the latter two had little effect on the lifetime, so these excitations have not been included for the other atoms.

Part of the  $f$  value program's [17] output is a short analysis table which identifies the largest (e.g.  $> 1\%$ ) contributions to the transition matrix element. In addition to the Dirac-Fock basis members, these were  $5p^5(5d + vd)$  and to a lesser extent,  $5p^5vs$  and  $5p^5vp$  ( $J = 0$ ). Now the separation between the two lowest  $J = 2$  roots ( $5p^55d$  and  $5p^56s$ ) was  $37\,310\text{ cm}^{-1}$ , much larger than the desired value of  $13\,255\text{ cm}^{-1}$ . What has happened is that we have preferentially correlated the ground state configuration  $5p^56s$  at the expense

of  $5p^55d$ . What is needed is to include the analogous medium and large energy contributors, marked with (T) above. Upon doing this, the bottom two roots are now separated by 15 669  $\text{cm}^{-1}$ , and the lifetime decreases to 48.3 s, which is the final value appearing in Table I. The  $J = 2$  wavefunction has 10 072 basis functions. The triples were added in stages, and at the last stage changed the lifetime in the 4th digit. For  $J = 0$  there are only 233 basis functions, because it is not necessary to include triples to correlate the  $5p^56p$  configuration, as it is a relatively small contributor to the lifetime. Inclusion of the Breit operator at the RCI level [18] had little impact on the Xe lifetime.

Table I includes our lifetimes of Ne, Ar, Kr and Rn as well. The experimental [16] excitation energy ( $J = 0 \rightarrow J = 2$ ) was always used. Based on Xe results, we did not excite from the  $d$  or  $s$  core subshells, nor include the Breit operator. The Ar and Kr results are in good agreement with available measurement. The A=222 isotope of Rn has  $I = 0$  and a nuclear lifetime of 3.82 days, so it would seem to represent the most favorable isotope to study. The result for Ne is somewhat lower than the MCDF value. Finally, we may expect that the more correlated the wavefunction is, without including the compensating triple excitations, the worse the lifetime result will be.

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- [1] H. Katori and F. Shimizu, Phys. Rev. Letts. **70**, 3545 (1993).
- [2] M. Walhout, A. Witte, and S.L. Rolston, Phys. Rev. Letts. **72**, 2843 (1994).
- [3] I.P. Grant, J. Phys. B **7**, 1458 (1974).
- [4] C.A. Nicolaides and D.R. Beck, Chem. Phys. Letts. **36**, 79 (1975).
- [5] J.P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).
- [6] C.A. Nicolaides and D.R. Beck, Can. J. Phys. **53**, 1224 (1975).
- [7] P. Westhaus and O. Sinanoglu, Phys. Rev. **183**, 56 (1969).
- [8] H.F. King, R.E. Stanton, H. Kim, R.E. Wyatt, and R.G. Parr, J. Chem. Phys. **47**, 1936 (1967).
- [9] A.T. Amos and G.G. Hall, Proc. Roy. Soc. (London) A **263**, 483 (1961).
- [10] C.A. Nicolaides and D.R. Beck, in “Excited States in Quantum Chemistry”, C.A. Nicolaides and D.R. Beck, editors, D. Reidel, Dordrecht, (1979), p. 143ff.
- [11] D.R. Beck, Phys. Rev. A **23**, 159 (1981).
- [12] D.R. Beck and Z. Cai, Phys. Rev. A **41**, 310 (1990).
- [13] P.L. Norquist and D.R. Beck, J. Phys. B **34**, 2107 (2001).
- [14] S. Fritzsche and C. Froese-Fischer, Comput. Phys. Commun. **99**, 323 (1997).
- [15] P.-O. Löwdin, Phys. Rev. **97**, 1490 (1955).
- [16] e.g. C.E. Moore, *Atomic Energy Levels* (U.S. GPO, Washington, DC, 1971), Vol. I.
- [17] D.R. Beck, Computer Code RFE (unpublished).
- [18] D.R. Beck, Computer Code RCI (unpublished).

TABLE I. Magnetic quadrupole lifetimes (s) for  $np^5(n+1)s$   $J = 2$  states.

Atom	SC-DF <sup>a</sup>	MCDF <sup>b</sup>	RCI <sup>c</sup>	Expt <sup>d</sup>
Ne	23.2	22	19.8	
Ar	47.4	51	32.2	38 (+8,-5)
Kr	63.2	63	35.0	39 (+5,-4)
Xe	101	96	48.3	42.4, 42.9
Rn	150		83.9	

<sup>a</sup> This work. Single configuration Dirac-Fock.

<sup>b</sup> Ref. [2]. Multi-configurational Dirac-Fock.

<sup>c</sup> This Work. Relativistic configuration-interaction.

<sup>d</sup> Experimental from refs. [1] and [2]. The two values for Xe correspond to different  $I = 0$  isotopes.