

## Resonance measurements of $d$ - $f$ and $d$ - $g$ intervals in lithium Rydberg states†

W. E. Cooke, T. F. Gallagher, R. M. Hill, and S. A. Edelstein

Molecular Physics Center, Stanford Research Institute, Menlo Park, California 94025

(Received 29 April 1977)

Using a laser-excitation, optical-detection scheme, we have observed microwave transitions from the  $nd$  to the  $nf$  and  $ng$  orbital levels in lithium states with principal quantum number  $n$  from 7 to 11. These measurements yield precise values for the  $d$ ,  $f$ , and  $g$  state fine-structure intervals as well as  $d$ - $f$  and  $d$ - $g$  energy separations. Within the accuracy of these measurements, the fine structures are found to be hydrogenic. The dipole polarizability of the  $\text{Li}^+$  core is determined from the  $d$ - $f$  and  $d$ - $g$  energy splittings. The  $d$ - $f$  intervals are compared to pseudopotential calculations.

### I. INTRODUCTION

While many of the properties of alkali atoms in Rydberg states are quite hydrogenic, the more subtle features of their spectra certainly are not. In particular, differences between the alkali and hydrogenic spectra arise due to effects of the finite size of the alkali core. The most obvious effect is the depression of the energies of the lower  $l$  states, which arises from the polarization and penetration of the core by the valence electron.<sup>1</sup> Less obvious, but equally dramatic, is the pronounced effect of the alkali ion core on the fine-structure (fs) intervals of excited states. In many cases the fine-structure intervals are inverted from the hydrogenic ordering.<sup>2</sup> To date, the finer details of only the sodium spectrum have been investigated in great detail. The  $\Delta l$  energy separations which were measured by Gallagher *et al.*<sup>3,4</sup> were used by Freeman and Kleppner to deduce the dipole and quadrupole polarizabilities of the  $\text{Na}^+$  core.<sup>5</sup> The polarizabilities of the ionic core deduced this way were found to be in fair agreement with *ab initio* calculations of Lahiri and Mukherji.<sup>6</sup> Since the  $\text{Li}^+$  ion is a much simpler system than the  $\text{Na}^+$  ion, its properties can be calculated more precisely. Thus the value for the dipole polarizability of  $\text{Li}^+$  derived from lithium  $\Delta l$  energy separations reported here should afford a more fundamental check of such many-body calculations.

As mentioned earlier, the fine-structure intervals in alkali metals are well known to be nonhydrogenic in the lower  $l$  states. In the  $d$  states of Na, for example, the inverted fs is attributed to exchange-core polarization,<sup>7</sup> an effect which depends on the presence of  $l \neq 0$  electrons in the ionic core. Lithium is thus of particular interest since its core contains only two  $s$  electrons, and thus does not have the exchange-core polarization effects which are responsible for the inversion of the Na  $d$ -state fine-structure. Consequently, a close examination of the lithium fine-structure intervals provides an

excellent test of the validity of the exchange-core polarization treatment.

### II. EXPERIMENTAL PROCEDURE

The procedure used to measure the  $nd$ - $nf$  and  $nd$ - $ng$  intervals in lithium is basically the same as that used by Gallagher *et al.* to measure similar intervals in sodium.<sup>3,4</sup> As shown in Fig. 1, the

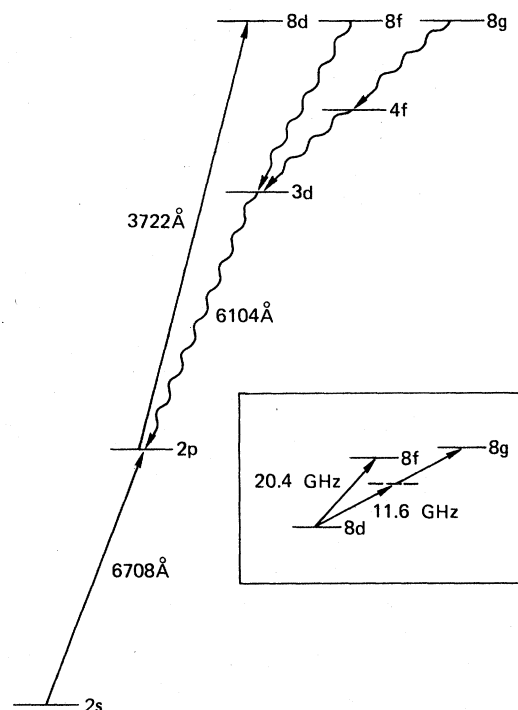


FIG. 1. Relevant energy levels for the observation of the  $8d$ - $8f$  and the  $8d$ - $8g$  transitions in lithium. The straight arrows are the two laser pumping steps; the wavy lines are the most probable decay channels. We observe the  $3d$ - $2p$  fluorescence at  $6104 \text{ \AA}$ . The inset shows the relative location of the  $d$ ,  $f$ , and  $g$  levels as well as the virtual level used in making a two-photon  $d$ - $g$  transition.

lithium atoms are pumped stepwise to an excited  $nd$  state by two tunable dye lasers, one at the 6709-Å resonance line, and a second at the  $2p \rightarrow nd$  transition (3600–3800 Å). Since the laser linewidth is slightly larger than the  $2p$  fine-structure interval, both  $p$  fine-structure states and, therefore, both  $d$  fine-structure states are populated. Microwaves induce a  $d$ - $f$  transition, or a  $d$ - $g$  transition, either of which results in an order of magnitude increase in the cascade fluorescence at the  $3d$ - $2p$  line (6104 Å).

The experiment was performed using an atomic beam of lithium, rather than a cell, because of the difficulties associated with the severe darkening of glasses caused by the hot lithium vapor.<sup>8</sup> The effusive oven was a 0.375-in.-diam, 0.007-in.-wall stainless-steel tube, with a  $0.005 \times 0.25$ -in. slit aperture. Approximately 75 A were passed through the oven to heat it to a temperature of approximately 800°C, producing a lithium density of  $\sim 10^{10}/\text{cm}^3$  in the interaction region.

To detect the  $3d$ - $2p$  radiation, we used an EMI 9558 phototube masked by an interference filter centered at 6100 Å with a 100 Å FWHM (full width at half maximum). In the absence of the microwave radiation, cascade transitions produced  $3d$ - $2p$  fluorescence so that the 3800-Å laser could be tuned using the phototube as a detector for Rydberg atoms in the  $nd$  state. Furthermore, although the resonance ( $2p \rightarrow 2s$ ) radiation was strongly attenuated by the filter, resonance radiation still registered at the phototube, allowing us to tune the 6709-Å laser.

Since the phototube surface is held at a high potential ( $\sim -1$  kV), a copper screen was placed over its face to avoid broadenings and shifts in the resonances due to the Stark effect. Typically this grid was held at +2 V to cancel the residual electrostatic field from the photomultiplier tube in the interaction region.

The microwaves, which spanned several bands, were generated by one of several HP klystron oscillators in the 620 series, except for the 30 GHz power, which was generated by an HP 8690 BWO sweeper. The power was delivered to the interaction region via waveguide and a microwave horn, appropriate to the frequency band.

For frequency measurements at frequencies less than 18 GHz we used an HP 5340 A microwave counter. For higher frequencies, we employed a heterodyne system, in which a fixed-frequency local oscillator at approximately one half the desired frequency was doubled and mixed with the power oscillator which was swept through the resonance frequency. The difference ( $\sim 30$  MHz) was counted by a Systron-Donner 6151 counter, while the local oscillator frequency was recorded by the

HP 5340 A counter. This method produced an accuracy of better than 100 kHz.

The  $3d$ - $2p$  fluorescence was sampled by a PAR boxcar averager for 1  $\mu\text{s}$  after each laser pulse and recorded by one pen of a dual-pen recorder. The other pen recorded the frequency as the oscillator was swept by a motor. Sweeps were taken for both increasing and decreasing frequencies to cancel offsets produced by the boxcar time constant.

### III. RESULTS

For the  $d$ - $f$  transitions, measurements were obtained for the three transitions  $nd_{3/2} \rightarrow nf_{5/2}$ ,  $nd_{5/2} \rightarrow nf_{5/2}$ , and  $nd_{5/2} \rightarrow nf_{7/2}$  for states  $n = 7$ –10. As an example, the  $8d_{5/2} \rightarrow f_{7/2}$  transition is shown in Fig. 2. For  $n = 11$ , a clean line could only be observed for the  $d_{5/2} \rightarrow f_{7/2}$  line. The  $d$ - $g$  transitions were driven by a two-photon process for the  $n = 8$  and 9 transitions:  $nd_{3/2} \rightarrow ng_{7/2}$ ,  $nd_{5/2} \rightarrow ng_{7/2}$ , and  $nd_{5/2} \rightarrow ng_{9/2}$ . In Fig. 3, we show the  $9d_{5/2} \rightarrow 9g_{9/2}$  transition. For each transition the rf microwave power was varied over 9 dB, so that the frequencies could be extrapolated to zero power as in Fig. 4. The  $10d_{5/2} \rightarrow 10g_{9/2}$ ,  $11d_{3/2} \rightarrow 11g_{7/2}$ , and  $11d_{5/2} \rightarrow 11g_{9/2}$  transitions were driven by Stark mixing into the  $g$  state a small portion of  $f$  state character, with an electric field, thereby making a one-photon electric-dipole transition allowable.<sup>9</sup> The small residual electric field served the purpose of Stark mixing. Table I lists the measured frequencies for these transitions. The numbers in parentheses represent our estimates on one-standard-deviation confidence in the final digit.

The linewidth of a typical  $nd$ - $nf$  transition was 2 MHz, which is consistent with the Zeeman broadening due to the Earth's magnetic field. In the higher states ( $n = 10, 11$ ), the Stark effect of re-

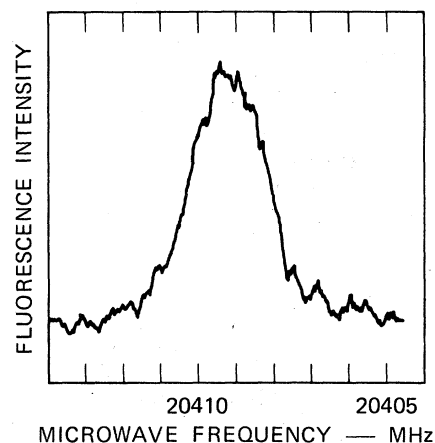


FIG. 2.  $8d_{5/2} \rightarrow 8f_{7/2}$  resonance on a sweep of decreasing frequency.

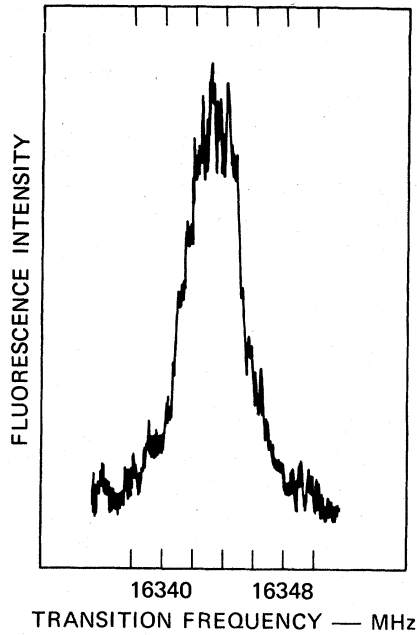


FIG. 3. Two-photon  $9d_{5/2}-9g_{9/2}$  resonance on a sweep of increasing frequency.

sidual stray electric fields resulted in some asymmetries in the resonances, typically less than 1 MHz.

The linewidths of the  $nd-ng$  transitions were noticeably larger, ranging from 3 MHz for the  $8d-g$  transition to 8 MHz for the  $11d-g$  transition. The added linewidth is due to Stark broadening from stray electric fields. We minimized the fields by varying the potential of the wire screen shielding the phototube and thus determined that the remaining shifts were of the order of the remaining Stark linewidth. The uncertainties quoted represent statistical uncertainties for the  $nd-nf$  transitions based on the reproducibility of the measurements, but for the  $nd-ng$  transitions the uncertainty is almost entirely due to the effects of stray electric fields.

#### IV. DISCUSSION

These measurements permit us to determine both fine-structure intervals and  $\Delta l$  intervals. The  $d$ ,  $f$ ,

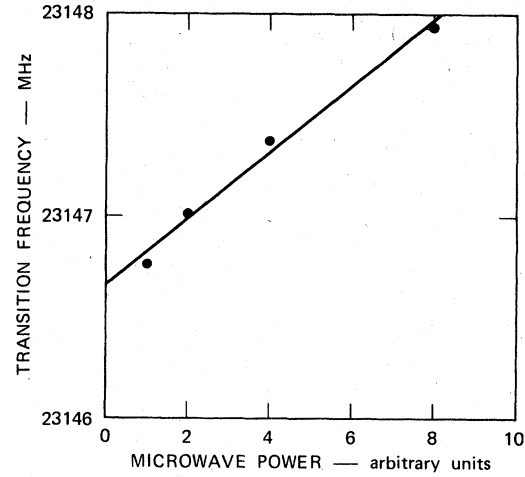


FIG. 4. Extrapolation of the two-photon  $8d_{3/2}-8g_{7/2}$  transition frequency to zero microwave power.

and  $g$  fine-structure intervals may be simply obtained from the difference of two transition frequencies:

$$\begin{aligned} S_d &= \nu_{d_{3/2}, f_{5/2}} - \nu_{d_{5/2}, f_{5/2}}, \\ S_f &= \nu_{d_{5/2}, f_{7/2}} - \nu_{d_{5/2}, f_{5/2}}, \\ S_g &= \nu_{d_{5/2}, g_{9/2}} - \nu_{d_{5/2}, g_{7/2}}. \end{aligned} \quad (1)$$

The Li fine-structure intervals determined in this way show no difference from hydrogenic theory.<sup>10</sup> In general, the fine structure of alkali atoms becomes more hydrogenic with increasing  $l$ ; thus, since the lithium  $d$ -state fine structure is so nearly hydrogenic [within 1% using Eq. (1)], we may safely assume the  $f$ -state fine structure is hydrogenic and use the stronger  $\Delta J=1$  transitions to obtain a better value for the  $d$ -state fine-structure interval:

$$S_d = \nu_{d_{3/2}, f_{5/2}} - \nu_{d_{5/2}, f_{7/2}} + S_f. \quad (2)$$

(As an example of the validity of this assumption, the sodium  $d$ -state fine-structure interval differs from hydrogen by  $\sim 300\%$ , whereas the  $f$ -state fine-structure interval is within 5% of hydrogenic theory.<sup>11</sup>) In Table II, we list the Li  $f$  and  $g$  fs intervals obtained using Eq. (1) and the  $d$  fs intervals

TABLE I. Transition frequencies (MHz).

$n$	$d_{3/2} \rightarrow f_{5/2}$	$d_{5/2} \rightarrow f_{5/2}$	$d_{5/2} \rightarrow f_{7/2}$	$d_{3/2} \rightarrow g_{7/2}$	$d_{5/2} \rightarrow g_{7/2}$	$d_{5/2} \rightarrow g_{9/2}$
7	30 235.31(30)	30 151.04(50)	30 193.03(30)			
8	20 437.67(30)	20 381.18(30)	20 409.23(30)	23 156.92(60) <sup>a</sup>	23 100.52(60) <sup>a</sup>	23 117.56(60) <sup>a</sup>
9	14 440.08(30)	14 400.12(30)	14 420.08(30)	16 370.8(10) <sup>a</sup>	16 330.6(10) <sup>a</sup>	16 342.7(10) <sup>a</sup>
10	10 572.64(50)	10 545.1(10)	10 558.61(50)	...	...	11 960.8(30) <sup>b</sup>
11	...	...	7 956.3(10)	9 025.5(50) <sup>b</sup>	...	9 009.4(50) <sup>b</sup>

<sup>a</sup> Measured by two photon resonance.

<sup>b</sup> Measured by Stark mixing.

TABLE II. Theoretical ( $S_{lt}$ ) and experimental ( $S_{lx}$ ) fine-structure splittings (in MHz) of the  $d$ ,  $f$ , and  $g$  sublevels of lithium.

$n \setminus l$	$d$		$f$		$g$	
	$S_{dt}^a$	$S_{dx}^b$	$S_{ft}^a$	$S_{fx}$	$S_{gt}^a$	$S_{gx}$
7	85.18	84.87(60)	42.59	41.99(80)		
8	57.07	56.97(60)	28.53	28.05(60)	17.1	17.0(12)
9	40.08	40.04(60)	20.04	19.96(60)	12.0	12.1(20)
10	29.22	28.6(10)	14.61	13.6(15)		

<sup>a</sup> Calculated from hydrogenic theory (Ref. 10).

<sup>b</sup> Calculated from  $\Delta J=1$  transitions, assuming hydrogenic  $f$ -state fine structure.

obtained using Eq. (2). The theoretical values for hydrogen are given for comparison.

Sternheimer *et al.* have suggested that the radical departure of heavier alkali fine-structure intervals from hydrogenic theory is due primarily to exchange-core polarization, which depends on the presence of  $p$  electrons in the alkali-ion core.<sup>7</sup> By comparing the Li  $d$  fs with the Na  $f$  fs we can check this hypothesis. In both the Li  $d$  states and the Na  $f$  states, the core polarization and penetration effects are comparable, resulting in similar quantum defects of 0.0019 and 0.0015, respectively. The major difference is the presence of  $p$  electrons in the Na<sup>+</sup> core, whereas there are only  $s$  electrons in the Li<sup>+</sup> core; however, the Na  $f$  fs intervals have been shown to be 5% lower than hydrogenic theory,<sup>11</sup> while here we have found that the Li  $d$  fs intervals are within 0.5% of hydrogenic theory. It is thus reasonable to attribute the departure of Na  $f$  fs from hydrogenic theory to exchange core-polarization effects present in Na but absent in Li.

Using the transition frequencies of Table I, and hydrogenic fine-structure intervals, we have calculated the separations of the centers of gravity of the  $nd$ ,  $nf$ , and  $ng$  levels (Table III) which are the  $\Delta l$  intervals. A comparison of the best previous measurements of the  $d$ - $f$  intervals for  $n=7-9$ , obtained from spectroscopic measurements,<sup>12</sup> is presented with our measured  $d$ - $f$  intervals in Table IV. We could find no previous measurements of  $d$ - $g$  intervals.

TABLE III. Separation (in MHz) of the centers of gravity of the  $nd$  and  $nf$  levels and the  $nd$  and  $ng$  levels.

$n$	$d$ - $f$	$d$ - $g$
7	30 208.84(20)	•••
8	20 419.88(20)	23 132.21(50)
9	14 427.52(20)	16 353.38(100)
10	10 564.01(40)	11 968.6(30)
11	7 960.4(10)	9 015.6(50)

Freeman and Kleppner have used similar intervals of sodium to calculate  $\alpha'_d$  and  $\alpha'_g$ , the dipole and quadrupole polarizabilities of Na<sup>+</sup>, using an adiabatic approximation.<sup>5</sup> Following their algorithm, one attributes the  $\Delta l$  splittings to a perturbation potential:

$$V' = -\frac{1}{2} \frac{\alpha'_d}{r^3} - \frac{1}{2} \frac{\alpha'_g}{r^5} \text{ (a.u.)}. \quad (3)$$

The expectation values of this perturbation (assuming hydrogenic Rydberg wave functions) produce energy shifts for each of the  $l$  states. The differences between these shifts are the  $\Delta l$  intervals. Having both  $d$ - $f$  and  $d$ - $g$  splittings for  $n=8-11$ , we may solve Eq. (3) for  $\alpha'_d$  and  $\alpha'_g$  of Li<sup>+</sup> in the adiabatic approximation:

$$\alpha'_d = 0.0279(3) \text{ \AA}^3, \quad \alpha'_g = 0.0019(3) \text{ \AA}^5. \quad (4)$$

The uncertainty of these values is due to the effects of core penetration on the level separation. The polarizabilities were calculated assuming no core penetration, and the resulting error was estimated using a first-order Ritz variation method approximation for the core electron density,<sup>13</sup> which yields  $\Delta E_{\text{pen}} \sim 10^{-5} n^{-3}$  (a.u.).

TABLE IV. Experimental and theoretical determinations of the separation (in GHz) of the centers of gravity of the  $nd$  and  $nf$  levels.

$n$ <sup>a</sup>	Expt.	Prev. expt. <sup>b</sup>	Theoret. <sup>c</sup>
7	30.2088	31.8	35.5
8	20.4199	23.7	23.8
9	14.4275	16.2	16.7
10	10.5640		12.2
11	7.960		9.14

<sup>a</sup> Theoretical quantum defects were reported for  $E = -0.006$  a.u. ( $n=9$ ); we have calculated the intervals for  $n=7-11$  using these quantum defects.

<sup>b</sup> Spectroscopic results (Ref. 12).

<sup>c</sup> Obtained by integrating Schrödinger's equation assuming a pseudopotential (Ref. 17).

These values must be corrected for nonadiabatic effects before they can be compared to many-body calculations. Eissa and Öpik have calculated the nonadiabatic corrections for selected sodium and potassium states.<sup>14</sup> The dipole polarizability is only slightly different from  $\alpha'_d$  (3% for K, 0.5% for Na), so that the correction in Li should be of the order of 1%. In fact, the *ab initio* calculation of Cohen,<sup>15</sup>  $\alpha_d = 0.0280 \text{ \AA}^3$ , is in excellent agreement with our measurements. On the other hand, the difference between  $\alpha_Q$  calculated for a nonadiabatic system and  $\alpha'_Q$  is typically quite large, for Na,  $\alpha_Q \approx 3\alpha'_Q$ ; for K,  $\alpha_Q \approx 4\alpha'_Q$ . Although the nonadiabatic corrections have not been calculated for lithium, our measured  $\alpha'_Q$  is approximately half as large as the calculated  $\alpha_Q$ , which is in qualitative agreement with the other alkali cases. (Lahiri and Mukherji<sup>16</sup> calculated  $\alpha_Q = 0.004648 \text{ \AA}^5$ .)

A somewhat more sophisticated potential including local "exchange" terms is commonly used to describe electron-atom scattering. Jaffé and Reinhardt have recently used these scattering potentials to calculate quantum defects.<sup>17</sup> In particular, for lithium they have used a core potential constructed from a static Hartree-Fock term,<sup>18</sup> a semiclassical exchange approximation,<sup>19</sup> and a polarization term.<sup>20</sup> Using this assumed potential, they numerically integrated Schrödinger's equation to calculate quantum defects. Using these reported

quantum defects we have calculated the  $\Delta l$  splittings. Table IV compares the calculated *d-f* intervals with our observed intervals. It is worth noting that whereas the earlier measurements exhibited excellent agreement with the calculated values, the improved measurements display a 16% difference. This difference must be a reflection of the choices of polarization potential, which had been obtained by fitting the lithium optical spectra,<sup>20</sup> since the other two potential terms are from *ab initio* calculations. Presumably, one could adjust the polarization term for a better fit to the high-*n* *d-f* and *d-g* intervals, which are determined primarily by core-polarization effects, and with this improved potential make a more precise check of the core-interaction model by calculating *p*-state quantum defects. At present the calculated *p* quantum defects disagree with experiment by more than 20%; however, the large error in the polarization term masks errors in either of the two *ab initio* terms. The use of a more accurate polarization term should allow a sensitive test of the *ab initio* terms.

#### ACKNOWLEDGMENTS

We would like to acknowledge the generous loans of microwave equipment by S. Tetenbaum, J. Watgen, G. Tomlin, and W. Bischel.

†Work supported by SRI Internal Research and Development funds.

<sup>1</sup>E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1964), p. 141.

<sup>2</sup>C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Circ. No. 467 [U.S. GPO, Washington, D. C., 1949 (Vol. I), 1952 (Vol. II), 1958 (Vol. III)]. See also K. H. Liao, L. K. Lum, R. Gupta, and W. Happer, *Phys. Rev. Lett.* **32**, 1340 (1974).

<sup>3</sup>T. F. Gallagher, R. M. Hill, and S. A. Edelstein, *Phys. Rev. A* **12**, 1464 (1975).

<sup>4</sup>T. F. Gallagher, R. M. Hill, and S. A. Edelstein, *Phys. Rev. A* **14**, 744 (1976).

<sup>5</sup>R. R. Freeman and D. Kleppner, *Phys. Rev. A* **14**, 1614 (1976).

<sup>6</sup>J. Lahiri and A. Mukherji, *Phys. Rev.* **153**, 386 (1967).

<sup>7</sup>R. M. Sternheimer, J. E. Rodgers, T. Lee, and T. P. Dash, *Phys. Rev. A* **14**, 1595 (1976); T. Lee, J. E. Rodgers, T. P. Das, and R. M. Sternheimer, *Phys. Rev. A* **14**, 51 (1976).

<sup>8</sup>P. Minguzzi, F. Strumia, and P. Violino, *Opt. Commun.*

**1**, 1 (1969).

<sup>9</sup>H. K. Hughes, *Phys. Rev.* **72**, 614 (1947); P. Zimmerman, T. W. Ducas, M. G. Littman, and D. Kleppner, *Opt. Commun.* **12**, 198 (1974).

<sup>10</sup>Reference 1, p. 120.

<sup>11</sup>T. F. Gallagher, W. E. Cooke, S. A. Edelstein, and R. M. Hill, *Phys. Rev. A* **16**, 273 (1977).

<sup>12</sup>I. Johansson, *Ark. Fys.* **15**, 169 (1958).

<sup>13</sup>H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic, New York, 1957).

<sup>14</sup>H. Eissa and U. Öpik, *Proc. Phys. Soc. Lond.* **92**, 556 (1967).

<sup>15</sup>H. D. Cohen, *J. Chem. Phys.* **43**, 3558 (1966).

<sup>16</sup>J. Lahiri and A. Mukherji, *Phys. Rev.* **141**, 428 (1966).

<sup>17</sup>C. Jaffé and W. Reinhardt, *J. Chem. Phys.* **65**, 4321 (1976); **66**, 1285 (1977).

<sup>18</sup>E. Clementi and C. Roetti, *Atm. Data Nucl. Data Tables* **14**, 177 (1974).

<sup>19</sup>M. E. Riley and D. G. Truhlar, *J. Chem. Phys.* **63**, 2182 (1975); **65**, 792 (1976).

<sup>20</sup>J. N. Bardsley, *Case Stud. At. Phys.* **4**, 301 (1974).