

## Absolute Calibration of Electric Fields Using Stark Spectroscopy

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We have established a direct link between laboratory electric fields and the atomic constants using Stark spectroscopy on  $n = 15$  sublevels of  ${}^7\text{Li}$ , coupled with an  $R$ -matrix theory of the Stark effect. Measurements are made with frequency-stabilized laser excitation by scanning the field from zero to above the saddle point. To estimate the zero-field energies we use quantum defect parameters from the polarization model for  $l \geq 4$ , and a fit to all available spectral data for  $l \leq 3$ . We claim that the electric field is known to about  $\pm 2 \text{ ppm} \pm 5 \text{ mV/cm}$ . Improvements and extensions are discussed.

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It should be possible to calibrate a static electric field to the accuracy of the relevant fundamental constants, but previous efforts have not been able to do this. The accuracy has been limited by the theory of the Stark effect in atoms, except for hydrogen (precision electric field experiments on single particles are impractical). By contrast, accurate calibration of magnetic fields by NMR, ESR, and other resonance methods is straightforward because the lowest order magnetic interaction often derives from the inherent dipole moment of fundamental particles. Magnetic fields acting on such particles produce a torque instead of a force, and the resulting precession frequency (energy shift) can be measured to high precision with resonance methods. The Schrödinger equation for this magnetic interaction is separable in spherical coordinates so the dipole moment can easily be calculated to first order. When combined with measurements, this provides accurate calibration.

Excited states of hydrogen have electric-field induced energy shifts that are calculable to high accuracy (the Schrödinger equation is separable in parabolic coordinates). Although accurate Stark experiments in H have been demonstrated [1–3], ppm accuracy has not been reported, due in part to experimental difficulties (dissociation of  $\text{H}_2$  into H atoms, excitation, high speed resulting from small mass). Alkali atoms are more easily handled experimentally, but the central potential is not precisely  $1/r$  so the Schrödinger equation is not separable. The problem of alkali atoms in an electric field has been addressed previously by notable theoretical efforts [4,5]. The most precise electric field calibration to our knowledge was performed on He atoms, using these same theories, and achieved error limits of  $\pm 50 \text{ ppm}$  [6]. In this Letter, we present results showing corroboration between experiments and a newly developed  $R$ -matrix

technique [7–9] to approximately 2 ppm in field, whereas the older methods are inaccurate by significantly larger amounts. The agreement is good enough to allow direct measurement of electric fields in terms of the fundamental constants.

Some years ago, extraordinarily sharp features in the Stark spectra of Rb associated with interference narrowing were found [10–13]. We [14] attempted to use these narrowings for a field calibration. Unfortunately, the measurements exhibited inconsistencies several hundred times larger than their internal precision [14]. After exhaustive studies of both the measurements and the theories used to interpret them, we changed from Rb to Li because of its much simpler electron core (no  $p$  or  $d$  electrons). When this change failed to resolve the discrepancies, we sought improvements in the theory.

The theory of the Stark effect in nonhydrogenic atoms presents a special type of nonseparable partial differential equation for the outer electron. The core region must be effectively excised from the solution since it constitutes a many-body problem. Outside the core itself, there is an effective potential (leading term  $r^{-4}$ ) caused by the polarization of the core by the outer electron. At sufficiently large  $r$ , core effects and also the major part of the relativistic mass correction term can be expressed to a high degree of accuracy by means of  $l$ -dependent quantum defects determining phase-shifted Coulomb wave functions.

The three theoretical methods we have tried each addresses this problem in fundamentally different ways. In the matrix diagonalization method [4], the electric field is treated as a perturbing element in a basis set of zero-field spherical eigenfunctions for various  $n, l$  states, with energies given by a quantum defect expansion. This method is necessarily truncated because only bound states

are included in the basis set. In the frame transformation method [5], WKB wave functions in parabolic coordinates are used for the outer region. Even after we modified it by using numeric wave functions, however, we found only small improvement in comparisons with experiment. In the  $R$ -matrix method [7–9], the phase-shifted spherical wave functions at small  $r$  are matched with eigenfunctions of the hydrogenic atom plus electric field at large  $r$ . The eigenfunctions are computed as combinations of spherical coordinate Sturmian functions, which provide great flexibility in meeting the boundary conditions as well as the desired long-range behavior. The application of this new method to our Li data has produced a high level of consistency.

The  $R$ -matrix theory splits space into two regions separated by a spherical surface of radius  $a$ . By choosing  $a$  large enough (we have used up to  $a = 20$  a.u.), one ensures that for  $r > a$ , the  $r^{-4}$  polarization potential and other core effects are negligible and thus that the potential is nearly exactly Coulombic. However, the wave functions are not hydrogenic because of core-induced phase shifts. Following recently developed procedures [7–9], we first consider the inner region, and express its solution at  $r = a$  in surface terms [15] related to phase-shifted Coulomb functions, to incorporate information about the region  $r < a$  into the outer problem. To achieve the level of accuracy needed here, we take into account effects of the external field in the inner region by adding surface terms off-diagonal in  $l$  caused by field mixing. The solution in the outer region is written as a sum of 800 to 2500 Sturmian functions with an optimized scaling parameter. In order to compute the properties of the resonances, especially above the saddle point, we use the “complex coordinate method” (or complex rotation of the Hamiltonian) so that the eigenvalues are made complex and the eigenfunctions square integrable. Finding the resonances at constant energy and at various field values then reduces to a generalized eigenvalue problem, which we solve using the Lanczos algorithm.

Our best field calibration results were obtained from direct spectroscopic measurements because we now use cw lasers. We have observed interference narrowing, but that technique is best suited to pulsed lasers in view of their inherent temporal resolution. We used two diode lasers to excite stepwise in a dc electric field from the  $2^2S$  ground state via  $2^2P_{3/2}$  to the  $3^2S$  state, and then a polarization-stabilized HeNe laser to excite Rydberg levels [16,17]. The HeNe laser is linearly polarized at  $45^\circ$  from the static field axis, so that both  $m = 0$  and  $m = \pm 1$  states can be excited (the latter states being degenerate). Data were obtained by scanning the electric field between two charged plates to shift the Stark levels into resonance with the HeNe laser frequency. The population of Rydberg atoms was measured by collecting ions through a slit in the bottom field plate, amplifying this signal with two microchannel plates, and counting

the pulses. Figure 1 shows data from a typical scan superimposed on a plot of energy levels of Li in an electric field.

Since we use no pulsed field to aid the ionization, the voltage applied to the electrode plate can be quite stable, thus facilitating precision measurements. A Keithley model 196 DVM (0.83 ppm/h accuracy) was used with a voltage divider to measure the top plate’s potential, and the field was scanned by changing the bottom plate’s potential from 0 to 10 V. This divider was made of five 20 M $\Omega$  and one 30 k $\Omega$  Caddock MG815 resistors (0.01 ppm/V accuracy). The scanning voltage was measured with the same voltage divider so that only one calibration factor is involved. Further details of the experiment are given in Refs. [16–18].

Resonance peak positions below and above the saddle point were measured. Above the saddle point, there is considerable field ionization broadening, so that most  $m = 0$  resonances were nearly 1 V wide. However,  $|m| = 1$  peaks are narrower because there is less core overlap and hence less core-induced coupling to continuum states. We determined the center location of each resonance by fitting a Gaussian to each ionization signal peak. This line shape closely approximates the experimental line shape, a Doppler broadened convolution of the natural and laser line shapes with typical linewidths of about 30 MHz. A typical photoionization signal obtained in a scan over a single peak is shown in Fig. 2. The experimental data in Fig. 2 exhibit some asymmetry caused by small drifts in the high voltage power supply and in the laser frequencies, and therefore the indicated uncertainty in the resonance position will be seen (below) to be too low.

To translate our theoretical results into laboratory units, we use the atomic units of energy and field obtained from the fundamental constants. For  $R_\infty$ , two recent experimental results [19] are far more accurate than we

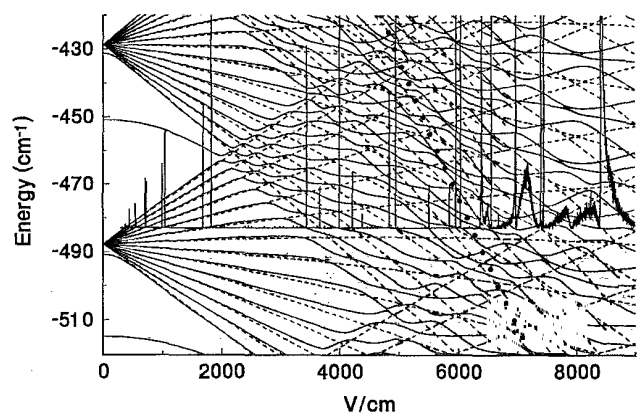


FIG. 1. Data obtained from a scan at  $E_0 = -483.06$  cm $^{-1}$  excitation energy from 0 to 9 kV/cm overlaid on a plot of Li energy levels. Solid lines and dashed lines denote  $m = 0$  and  $|m| = 1$  levels, respectively. Resonances appear when a sublevel is shifted to energy  $E_0$ . The saddle point energy is denoted by dots.

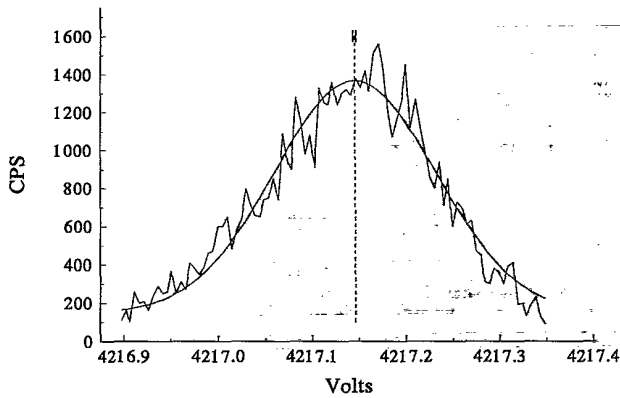


FIG. 2. Data from a scan over an individual resonance peak together with the fitted Gaussian function. The fitted resonance voltage and error bars are also shown. The data acquisition time for this scan was 10 sec.

need ( $1:10^{11}$ ), and for the field we use  $F_\infty \equiv e^2/a_\infty = 5.142\,2083(16) \times 10^9$  V/cm, where  $a_\infty \equiv \alpha/4\pi R_\infty$ . For the Rydberg electron of an atom with atomic mass  $M_A$ , the atomic unit of energy is  $2\rho_A R_\infty$  and the atomic unit of field is  $\rho_A^2 F_\infty$  where  $\rho_A = 1 - m_e/M_A$  ( $m_e$  is the electron mass). For  ${}^7\text{Li}$ ,  $\rho = (1 - 7.82) \times 10^{-5}$  and thus  $R_A({}^7\text{Li}) = 109\,728.735\,34$  cm $^{-1}$  and  $F_A({}^7\text{Li}) = 5.141\,404\,2(16) \times 10^9$  V/cm.

In addition to the constants, the Stark theory also needs accurate zero-field energies for Rydberg levels. We use a quantum defect (QD) expansion as defined in [20]. Zero-field energies are given by  $E(n, l) = -R_A/[n - \delta(l)]^2$ , where

$$\delta(l) = \delta_0 + \frac{\delta_2}{[n - \delta(l)]^2} + \frac{\delta_4}{[n - \delta(l)]^4} + \dots \quad (1)$$

For  $l = 4-14$ , QD parameters may be obtained from the polarization model [21] (including relativistic terms) that has been corroborated to a few kHz [22] by microwave experiments on  $n = 10$ ,  $l = 4-6$ . For  $l \leq 3$ , we obtain QD parameters from a fit to the available Li spectral data [22-28], which consists primarily of optical and IR measurements on low  $n$  levels and microwave measurements on high  $n$  levels. Fine structure parameters were fit but were not used in the present theory because their effect on the observed  $n = 15$  levels was not significant. A simultaneous fit of 140 transition frequencies to 20 QD parameters (set "A") for  ${}^2S$ ,  ${}^2P$ ,  ${}^2D$ , and  ${}^2F$  manifolds gave the lowest variance (rms ratio of residual to experimental error) of 2.8 while a fit to 16 QD parameters (set "B") yielded a variance of 9.1. The impact of uncertainties in the QD parameters on the field calibration is discussed below.

$R$ -matrix calculations are performed at two energies near the excitation energy estimated from the HeNe frequency. The 29 resonance field values from the data scans are fit to these calculations by varying this energy  $E_0$ , the effective plate spacing  $d$ , and a small voltage offset  $V_0$ . The last two parameters give the field from the

measured voltage. The Stark shift of the  $3^2S$  state, calculated by matrix diagonalization,  $R$ -matrix theory, or from the recently published polarizabilities [29] (the different methods agree to 0.2%), is included. The residuals between the  $R$ -matrix calculations and the results of these global fits are plotted in Fig. 3. The scatter is greater than the error limits for individual resonances because of small drifts in our voltage source and in the laser frequencies. From this fit, the uncertainty in the plate spacing and hence in the field is 1.5 ppm, while the uncertainty in the energy is 1 MHz. From various convergence tests, we believe the  $R$ -matrix calculations to be valid to about 0.1 ppm in field, but the effect of uncertainties in the zero-field energies and QD parameters must be considered.

The  $R$ -matrix method cannot easily accommodate the small quantum defect parameters for  $l \geq 8$  that arise from the relativistic mass correction term,  $E_{rel}$ , and the polarization potential [21]. These phase shifts accumulate primarily in the region  $r > a$ . Although we were obliged to neglect these shifts, we find that the average energy shift from these omitted quantum defect parameters is mostly canceled (to  $\approx 1$  MHz) by the positive energy shifts from the  $n^{-4}$  part of  $E_{rel}$ , which is not included in the QD shifted energies [30]. The net effect on the fitted effective plate spacing is only  $\approx 0.4$  ppm.

The effect of uncertainties in the  $l \leq 3$  QD parameters is indicated by two tests. The difference in the fitted field calibration obtained from QD parameter sets A and B was 0.4 ppm. Varying the parameters in each set to the error limits of the respective fits, produced a change of  $\approx 0.1$  ppm in the fitted value of  $d$ .

Taking into account these small corrections, we claim a calibration of laboratory electric field in terms of atomic constants accurate to about 2 ppm plus an uncertainty of 5 mV/cm from  $V_0$ . This method does not depend on detailed knowledge of experimental geometry

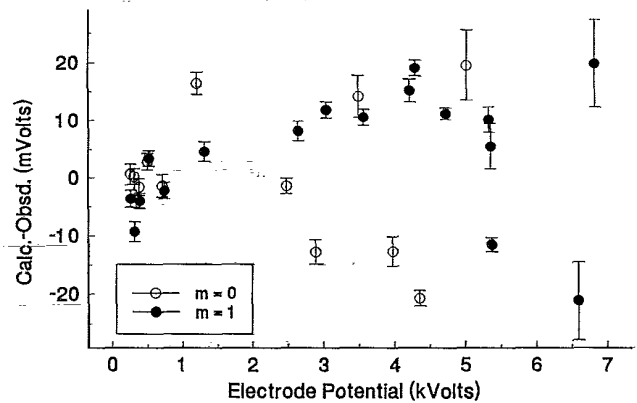


FIG. 3. Residuals from a fit of 29 measured resonances to  $R$ -matrix calculations. The  $m = 0$  (open circles) and  $|m| = 1$  (closed circles) data were fit together. The calibration parameters obtained from the fit are  $d = 0.723\,717\,6(10)$  cm, offset voltage,  $V_0 = 0.294(4)$  V, and  $E_0 = -483.060\,778(30)$  cm $^{-1}$ .

or laser frequency, but does depend heavily on theoretical accuracy.

This level of precision in the measurement of an electric field raises other possibilities. If the experiment were performed with a stabilized HeNe laser of known frequency, the binding energy of the Li  $3^2S$  state could be determined to within  $\approx 1$  MHz by adding the laser energy and the fitted upper level energy. This could be used to test calculations on relativistic and QED effects in Li, since the nonrelativistic energies are accurately known [31]. If an independent measure of the effective plate spacing could be made to comparable precision, including contact potentials, domain differences, etc., then one would have a measure of  $e$ , the charge of the electron (assuming a Josephson junction measure of the voltage). We believe the theory is capable of 0.1 ppm accuracy and that the experimental technique could be extended to this level with the help of a stabilized voltage supply and better frequency-stabilized lasers. However, it may be that hydrogen atoms would be more suitable for a determination of  $e$ .

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