Rydberg states of atoms in parallel electric and magnetic fields

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We present theoretical results for the photoabsorption spectrum of an atom in parallel electric and magnetic fields, using the *R*-matrix method combined with quantum-defect theory. We introduce a radial basis set which is complete and orthonormal over a semi-infinite interval $[r_0, \infty)$, to allow calculations to be performed for high Rydberg states in nonhydrogenic atoms without encountering problems due to linear dependence of the basis set. The nonhydrogenic character of the spectra is analyzed for Li and Rb, and a comparison is made with previous high-precision experiments which shows that the theoretical results agree very well with experiment. [S1050-2947(99)06002-3]

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A Rydberg atom in parallel electric and magnetic fields is an interesting extension of a Rydberg atom in a magnetic field [1–3], whose spectrum has been well studied both experimentally and theoretically. Experimentally, even for an atom in a magnetic field there is usually a weak stray electric field present so it is important to know how it affects the spectrum. From a theoretical point of view the problem remains nonseparable [4], as for an atom in a magnetic field, but there is a reduction of symmetry brought in by the additional applied electric field. Theoretical quantum-mechanical calculations [5,6] have been mainly confined to the use of perturbation theory in the photoabsorption part of the spectrum while resonance energies in the continuum have been calculated by the complex-coordinate method [7]. High-resolution experiments [6] have been performed for the photoabsorption spectrum of atoms in parallel fields for different field intensities and for different atoms. Due to the breakdown of *z*-parity induced by the presence of the electric field, the nonhydrogenic character of the atoms is generally more significant than in the magnetic field case as all of the quantum defects can affect the spectrum.

We present in this Brief Report an *ab initio* quantum-mechanical calculation of photoabsorption spectra of Rydberg atoms in parallel electric and magnetic fields over a large spectral range going from well defined manifolds in the inter-*l* mixing region to spectral regions where inter-*n* mixing is observed and where perturbative theories no longer apply. We use a variant [8–10] of the *R*-matrix method [11], in which the system's wave function is expanded in a basis-set of radial functions defined so that they are orthogonal over a semi-infinite region $[r_0, \infty)$. The introduction of such a radial basis set which is orthogonal over the semi-infinite interval $[r_0, \infty)$ avoids the linear dependency problems found in earlier caculations using a Sturmian base, particularly if r_0 is chosen to be large. We use the method to analyze the nonhydrogenic behavior exhibited in the photoabsorption spectra of Li and Rb by comparing with hydrogen for one particular manifold in the inter-*l* mixing region of the spectrum and we compare the theory with experiment. We then extend this analysis to higher energies into the inter-*n* mixing region and close to the electric field ionization limit.

The nonrelativistic Hamiltonian of a hydrogen atom subject to externally applied parallel electric and magnetic fields oriented along the *z* axis (assuming an infinite proton mass), in atomic units and spherical coordinates, is given by

$$H = H_0 + H_p + H_d + H_f$$
$$= -\frac{1}{2}\nabla^2 - \frac{1}{r} + \beta L_z + \frac{1}{2}\beta^2 r^2 \sin^2\theta + fr\cos\theta, \quad (1)$$

where $\beta = B/B_c$ ($B_c = 4.7 \times 10^5$ T) and $f = F/F_c$ ($F_c = 5.14 \times 10^9$ V cm^{-1}) express the magnetic-field and electric-field strengths respectively, in atomic units. The first two terms on the right-hand side of Eq. (1) represent the zero-field Hamiltonian H_0. As the Hamiltonian has rotational symmetry around the *z* axis, the component L_z of the orbital angular momentum in the field direction is a conserved quantity but parity with respect to the $z=0$ plane is not conserved. It is then possible to label the corresponding eigenfunctions with a fixed value of the magnetic quantum number *m*. In a subspace of a given *m*, the paramagnetic interaction H_p only introduces a uniform shift of βm in the energy levels.

The effect of the diamagnetic and electric potential terms, respectively H_d and H_f, on the motion of an electron depends on the strength of the external fields and on the radial extent of the electron from the nucleus. For typical laboratory field strengths, as the electron moves in higher radial Rydberg states, the H_d and H_f potentials become comparable to the Coulomb field and perturbation theory can no longer be applied; the Schrödinger equation must be solved directly. Although the Schrödinger equation for the pure Stark effect ($\beta = 0$) is separable in parabolic coordinates [$\eta = r - z$, $\xi = r + z$, $\phi = \arctan(y/x)$], the corresponding Schrödinger equation for the hydrogen atom in a pure magnetic field ($f = 0$) is nonseparable, as a result of the coexistence of a spherically symmetric Coulomb potential and a cylindrically symmetric diamagnetic potential in the Hamiltonian for such a system. Consequently, the difficulty associated with the motion of an electron in an atom in external parallel electric and magnetic fields lies in the nonseparability of the corre-

sponding Schrödinger equation with the Hamiltonian (1) exhibiting the different symmetries of each of the potentials present.

For a general atom the H_0 term in Eq. (1) has to be modified to include the effect of the atomic core while the other terms represent the effect of the potential seen by the Rydberg electron outside the core. The corresponding Schrödinger equation is solved by using an original idea based on using quantum-defect theory [12] to describe the interaction of the Rydberg electron with the ionic core and the R-matrix method to solve the Schrödinger equation over the semi-infinite region outside the core [8–10]. The reader is referred to Refs [8–10] for details. For alkali metals, core effects are represented by the quantum defects μ_l, associated with the corresponding lth partial wave. We solve the Schrödinger equation over the semi-infinite region outside the core by using a radial basis set $F_n(r)$ which has the advantage of being complete and orthogonal over a semi-infinite interval $[r_0, \infty)$. Such an orthonormalized basis set is obtained by defining the set in terms of Laguerre polynomials in the following way:

$$F_n(r) = \sqrt{\xi} e^{-\xi/2(r-r_0)} L_n[\xi(r-r_0)]. \quad (2)$$

ξ is a parameter which can be varied to vary the radial extent of the basis set and to test convergence. r_0 may be arbitrary but should be larger than the core radius.

In Fig. 1 we present theoretical spectra for H, Li, and Rb, calculated for external parallel electric and magnetic fields of $F = 15$ V cm^{-1} and $B = 2.33$ T, respectively, in the inter-l mixing region and including several manifolds beginning with $n = 29$. The atoms are excited with π-polarized light from the ground initial state $l = 0$, $m = 0$. Oscillator strengths are relative and plotted against energy referred to the zero-field ionization limit. Comparison between the hydrogen spectrum and lithium and rubidium shows that the nonhydrogenic character of the core strongly affects the lower energy part of each of the manifolds. At field strengths sufficiently weak for n to remain an approximately good quantum number, one and two lines for Li and Rb, respectively, stand out from the rest of the manifold because of the quantum defects and nondegeneracy of the lowest l's. Li has a significant $l = 0$ quantum defect ($\delta_0 = 0.40$) and for Rb the $l = 1$, 2 quantum defects are also significant ($\delta_0 = 0.14$, $\delta_1 = 0.35$, $\delta_2 = 0.34$) [13] (All quantum defects are given modulo 1). The overall appearance of the upper energy part of the manifold remains similar. The features present in Li were already discussed by Cacciani et al. [6]. The lower energy part of the manifold is associated with vibrational states while the upper part is associated with rotational states. The vibrator part of the spectrum is strongly affected by the applied electric field while the rotator part retains its main features for the values of fields and n used. This can be understood as follows. For hydrogen in zero electric field in the l-mixing region, it was shown [14–16,6] that the quantity $\Lambda = 4A^2 - 5A_z^2$ is a constant of the motion, for $\mathbf{A}$ the Runge-Lenz vector and A_z its z component. Vibrational states correspond to negative values of Λ, hence $\mathbf{A}$ moves on a twofold hyperboloid with two preferential orientations either parallel or anti-parallel to the direction of the magnetic field—this gives the twofold degeneracy of odd and even parity states in hydrogen. For ro-
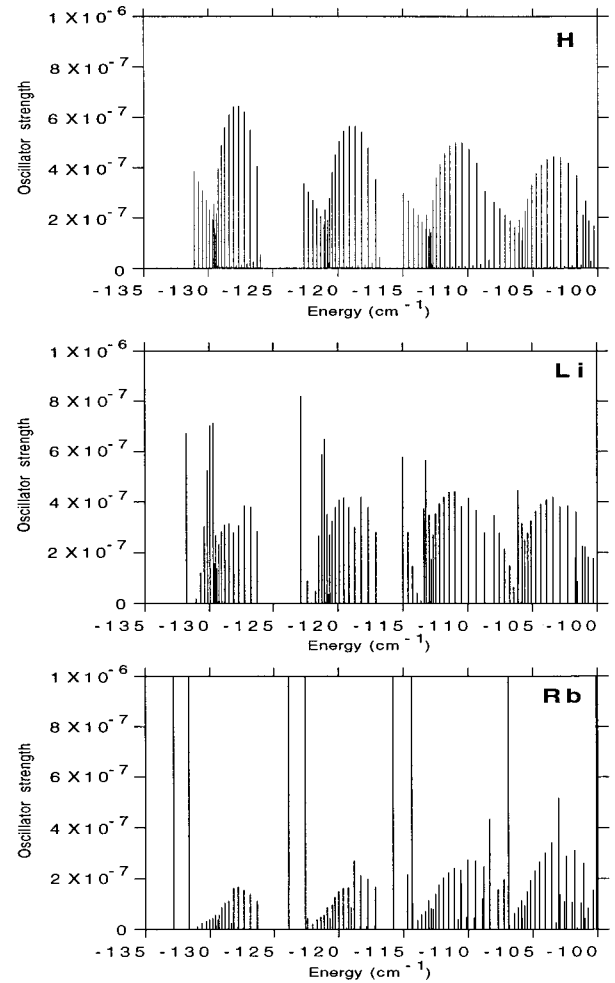

FIG. 1. Theoretical photoabsorption spectra for hydrogen, lithium, and rubidium in the presence of parallel electric and magnetic fields of $F = 15$ V cm^{-1} and $B = 2.33$ T for an energy region starting from the $n = 29$ manifold. The high intensity lines in the spectrum decrease monotonically from 3.8×10^{-6} until 2.6×10^{-6}. The oscillator strength is dimensionless and relative. The transition studied is from the ground initial state $s, m = 0$ using π-polarized light.

tator states Λ is positive and the Runge-Lenz vector moves on a onefold hyperboloid with no preferential orientation. It is then clear that the vibrational states have a nonzero electric dipole moment while rotational states do not. As a consequence, in parallel electric and magnetic fields, the vibrational states of the manifold exhibit a linear Stark splitting and are strongly affected by the electric field whereas the rotational states present a quadratic Stark effect. This is observed as long as the electric field strength is sufficiently small.

In Fig. 2 we compare theoretical results showing the evolution of the $n = 30$ lithium manifold in the presence of a fixed magnetic field of $B = 2.33$ T and increasing values of applied electric fields, as observed experimentally by Cacciani et al. [6]. The atoms were excited with π-polarized light from the ground initial state ($l = 0$, $m = 0$) and the relative strength of the Stark and diamagnetic effects within an n manifold can be measured by the parameter γ defined by $\gamma = 3f/5\beta^2 n^2$. The theoretical calculation successfully reproduces the experimental data showing manifolds with the fea-
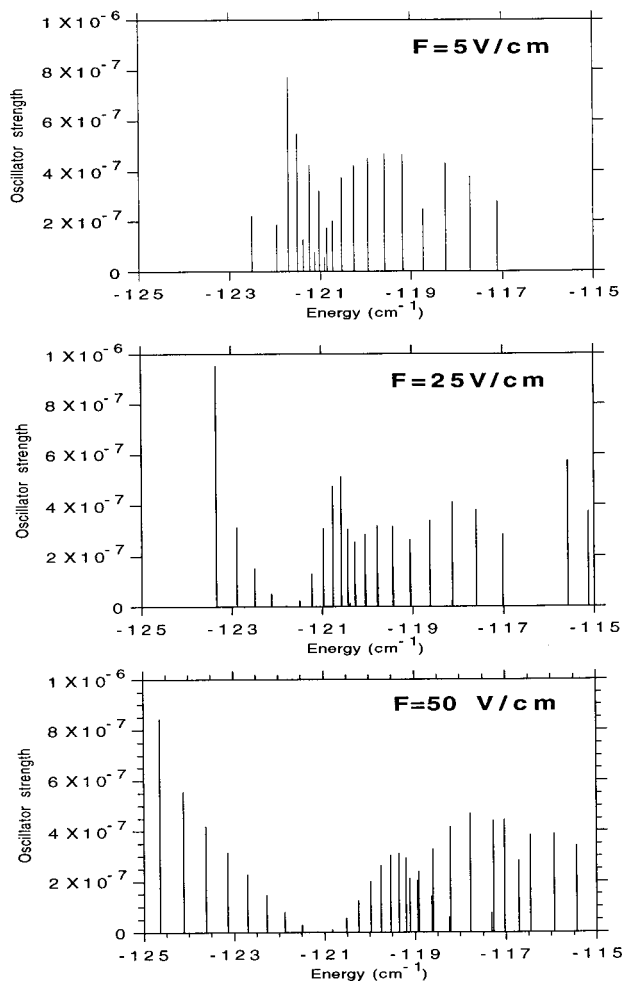
FIG. 2. The calculated photoabsorption spectrum of lithium showing the evolution of the manifold corresponding to $n=30$, for parallel electric and magnetic fields, when the magnetic field is kept constant at 2.33 T and the static electric field, F, is varied as indicated. For $F=50$ $V\,cm^{-1}$ the higher energy part of the manifold mixes with the $n=31$ manifold.
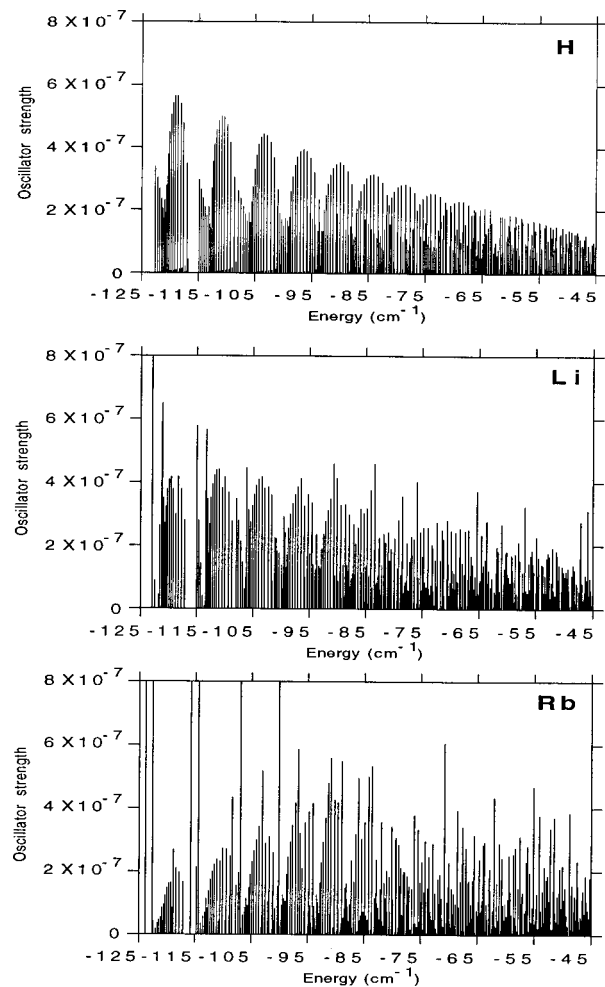
FIG. 3. Theoretical photoabsorption spectra for hydrogen, lithium, and rubidium in parallel electric and magnetic fields with the same parameters as in Fig. 1 over a larger range of energies, including regions where complex structure is observed.

tures described above. With increasing electric field, larger γ, the total number of vibrational states increases, due to the fact that rotational states become gradually vibrational states. As a result, the lower energy part presents a gradually more pronounced Stark structure with energy levels equally spaced and oscillator strengths decreasing monotonically; rotational states exhibit a transition from the quadratic to the linear Stark effect with increasing field strength.

In Fig. 3 we show theoretical spectra obtained for the three atoms we have been considering, H, Li and Rb, for the same field parameters as in Fig. 1 but a range of energies going up to -45 cm^{-1}. It can be seen that the nonhydrogenic character of the spectra is mostly reflected by the presence of the high intensity shifted lines of the spectra which correspond to the lower l components of the wave function penetrating the core. This feature becomes less dominant when entering the inter-n mixing region; the inter-l mixing regime is initially not fundamentally modified when the manifolds overlap until the spectra display a more complex

structure from about 60 cm^{-1} on. This region corresponds to an energy region where classically chaos sets in.

In summary, we present *ab initio* quantum-mechanical calculations for the photoabsorption spectra of Rydberg atoms in parallel electric and magnetic fields, using a orthonormal basis set defined over a semi-infinite interval. Excellent agreement was obtained with previous experimental results published by Cacciani *et al.* in the inter-l mixing region. The method also allows one to study the inter-n mixing region and we show that the spectra are dominated by states with lower l and high quantum-defect values as long as the field strengths are weak enough with respect to the Rydberg levels considered. The results are easily extended to the field ionization threshold by using larger basis sets.

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