Continuum Spectrum of an Atom or Molecule in a Magnetic Field

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We calculate the positive-energy spectrum of both hydrogen and lithium atoms in a field of 6.1 T and we show how such spectra can be obtained for an atom or molecule in an arbitrary strength magnetic field. The theory combines quantum-defect theory, *R*-matrix propagation, and two-dimensional frame transformations. Much of the resonance structure in the continuum can be understood in terms of complex perturbed Rydberg series.

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The subject of a Rydberg atom in a magnetic field has attracted a lot of attention, in part because of its connection with the question of nonintegrability and chaos in a Hamiltonian system [1]. There exists at the moment, detailed experimental spectra for both bound and continuum states of many atoms in laboratory strength fields of about 6 T [2]. Comparing theory and experiment for these systems has proved very difficult and until recently, the theoretical calculations had been confined to bound states.

We recently presented a general theory to calculate the bound and continuum states of any atom or molecule in an arbitrary strength magnetic field [3]. We initially applied the theory to the hydrogen atom in a very strong field of 470 T. However, as the experiments have been carried out at fields of 6 T, it is important to show that the theory can be applied at these field strengths so as to compare our results directly with experiment. We show in this Letter how this is achieved and we use the theory to calculate the continuum spectra of the hydrogen and lithium atoms in a field of 6.1 T. We also compare our results with the recent calculations [4] using the complex coordinate technique which are limited to the hydrogen atom in a magnetic field.

The difficulty associated with the motion of a Rydberg electron in a magnetic field arises from the competition between two potentials of different symmetry and the subsequent nonseparability of the Schrödinger equation. The Hamiltonian for the hydrogen atom in an external magnetic field which is taken to be pointing along the z axis is, in atomic units,

$$H=-\frac{1}{2}\nabla^2-\frac{1}{r}+\frac{\gamma}{2}l_z+\frac{1}{8}\gamma^2\rho^2 . \tag{1}$$

The external field adds an extra harmonic-oscillator potential in the cylindrical coordinate ρ, the quadratic Zeeman potential, to the field-free hydrogenic Hamiltonian. γ is the magnetic-field strength in atomic units and is usually very small, being 10^{-5} a.u. for a laboratory strength magnetic field of 2.35 T. l_z and parity under reflection about the x-y plane are conserved quantities so that we can confine our attention to eigenstates with a fixed value of m and parity. Hence the linear Zeeman term in (1) just gives rise to a uniform shift in the energy levels for a given m.

There are two readily identifiable asymptotic limits in which the above Hamiltonian is separable. As $r \rightarrow 0$ the equation is separable in spherical coordinates since the Coulomb potential dominates over the external field potential. In the opposite limit, i.e., as $z \rightarrow \infty$, the equation is again separable but now in cylindrical coordinates since

$$\begin{aligned} V(\mathbf{r}) &= -\frac{1}{(\rho^2+z^2)^{1/2}}+\frac{1}{8}\gamma^2\rho^2 \\ &\approx -\frac{1}{z}+\frac{1}{8}\gamma^2\rho^2+\frac{\rho^2}{2z^3}+O\left[\frac{1}{z^5}\right] \end{aligned} \tag{2}$$

with the motion in ρ being bounded due to the magnetic field. At intermediate values of r the Hamiltonian is nonseparable. This region marks the transition from spherical symmetry to cylindrical symmetry.

Except for our recent calculation [3] at 470 T all of the previous work, both for bound and continuum states [4], has been performed by expanding the wave function in a basis set of eigenfunctions expressed purely in either cylindrical or spherical coordinates. The number of eigenfunctions needed in such expansions can be vast, as one ends up trying to represent wave functions in regions of configuration space which have essentially cylindrical symmetry by using spherical expansions, or vice versa. The basis of our theory is to identify different regions of configuration space where particular forces and symmetries dominate and to solve the Schrödinger equation in these regions *separately* in the appropriate coordinate system. The solution over all space is then obtained by matching the solutions and their derivatives on the boundary surfaces between these regions.

The overall effect of the harmonic-oscillator potential in (1) on the motion of an electron depends *both* on the strength of the external field and on the radial extent of the electron from the nucleus or equivalently the excitation energy given to the electron. Thus, for $\gamma=10^{-5}$, the initial state in the photoionization process, namely, the ground or a low-lying excited state, is unaffected by the presence of the field since $\langle r\rangle$ or $\langle\rho\rangle\sim 1\text{-}10$ a.u. and so the magnetic potential, $\frac{1}{8}\gamma^2\rho^2$, is of the order of 10^{-9} which is a negligible perturbation to these states. However, the continuum states have an infinite radial extent in r and thus the electron moves in all of the three regions of configuration space described above. Hence for these states one has to pass from solutions expressed in spherical coordinates at short radial distances to solutions in cylindrical coordinates at large distances. Letting $\psi_\varepsilon(\mathbf{r})$ represent the wave function of the excited electron we divide configuration space into different regions. The first of these is a spherical region, $0\le r\le a$, where a is chosen large enough to contain the atomic or molecular core but small enough that the quadratic Zeeman potential in (1) is negligible. The electron is initially excited in this region and interacts with the other electrons in the core. Once it is outside the core, typically for $r\sim 10$ a.u., the electron is moving in the Coulomb field of the ion. So for $r>10$ a.u. one can write the lth partial wave function as

$$\psi_{\varepsilon l}(\mathbf{r})=[s_{\varepsilon l}(r)+c_{\varepsilon l}(r)\tan\pi\mu_l]Y_{lm}(\theta,\phi)\,, \tag{3}$$

where s and c are the regular and irregular Coulomb functions, respectively, and Y_{lm} are the spherical harmonics [5]. μ_l are the quantum defects and they represent the effect of the core on the excited electron's wave function. They can be calculated *ab initio* or deduced from experimental energy levels. Usually for $l>4$, $\mu_l=0$. The total wave function at $r=a$ can then in general be written as

$$\psi_\varepsilon(\mathbf{a})=\sum_l A_{\varepsilon l}\psi_{\varepsilon l}(\mathbf{a})\,, \tag{4}$$

where the A's are constants to be determined through matching to the asymptotic solutions. (For a molecule one may have to perform additional frame transformations at $r=a$, but otherwise everything follows in a similar way to the atomic case [6].)

When the electron moves beyond $r=a$ the magnetic potential in (1) is no longer negligible and the full potential is no longer Coulombic. We therefore consider a second spherical region $a\le r\le b$ where we expand the wave function for the excited electron in a spherical basis set as follows

$$\psi_k=\sum_{nl}c^k_{nl}\frac{f_{nl}(r)}{r}Y_{lm}(\theta,\phi)\,, \tag{5}$$

where the $f_{nl}(r)$ are a radial basis set of eigenfunctions. The eigenvectors c are determined by diagonalizing the Hamiltonian in (1) (plus the Bloch operator) over the finite region $a\le r\le b$ [7]. This enables one to construct a set of eigensolutions ψ_k of the Schrödinger equation in this region. The general solution is thus

$$\psi_\varepsilon(\mathbf{r})=\sum_k B_{\varepsilon k}\psi_k(\mathbf{r})\,, \tag{6}$$

where again the correct superposition coefficients B are determined by matching to the solutions at the boundary surfaces. Beyond $r=b$ the electron is moving in the asymptotic zone and the symmetry is essentially cylindrical.

We therefore choose the third region to be cylindrical with $c\le z\le d$ and $0\le\rho<\infty$. (This region overlaps the spherical region $a\le r\le b$ since we will match the cylindrical solutions with the spherical solutions at $r=b$.) We take the boundary at $z=d$ to be large enough that the potential can be approximated by its separable limit in (2). Then one can write down the following analytic expression for the jth linearly independent solution in cylindrical coordinates in the region $d\le z<\infty$,

$$\psi_{\varepsilon j}=\sum_i\Phi_i(\rho,\phi)[s_i(z)\delta_{ij}+c_i(z)K_{ij}]\,, \tag{7}$$

where Φ_i denotes the ith Landau or harmonic-oscillator level, s_i and c_i are the regular and irregular Coulomb functions, and K_{ij} is the reactance matrix. In the region $c\le z\le d$ we keep, in addition, the first coupling term in (2) which is of the order $1/z^3$. Although these couplings are small they cause significant perturbations since the electron is moving very slowly. We again use a basis set expansion or the R-matrix method as in (5) but this time using a set consisting of a product of Landau states Φ_i and a radial basis set in z. Thus knowing the regular and irregular solutions at $z=d$ from (7) we can obtain the corresponding coupled-channel solutions over the whole region $c\le z\le d$, namely,

$$\psi_{\varepsilon j}=\sum_{ik}\Phi_i(\rho,\phi)[S_{ij}(z)+C_{ik}(z)K_{kj}]\,. \tag{8}$$

We now have a set of linearly independent solutions over all space but expressed in different regions and in different coordinate systems. The final step is to match these solutions and to calculate the K matrix.

Since we know the logarithmic derivative or R matrix (the inverse of the logarithmic derivative), $R_{ll'}$, at $r=a$ from (3), we can calculate the R matrix at $r=b$ from the solutions in (5), i.e., we can propagate the R matrix from $r=a$ to $r=b$ [7]. The calculated R matrix at $r=b$ contains many unwanted channels. A key point is to eliminate these channels. We first calculate the local adiabatic solutions by diagonalizing the Hamiltonian in (1) at fixed $r=b$ in a basis set of spherical harmonics. The corresponding solutions are $\phi_\lambda(\theta,\phi)$. We then perform a frame transformation from the basis set of spherical harmonics to the new local adiabatic set at $r=b$. The R-matrix $R_{ll'}$ is thus transformed to $R_{\lambda\lambda'}$ and can be contracted to the number of channels of physical interest, i.e., the number of Landau channels. The ϕ_λ are bounded in ρ and are similar to the Landau states. We then evaluate the regular solutions in (8) on the arc $r=b$ and project these solutions onto the ϕ_λ, i.e., we integrate over θ and ϕ, giving

$$F_{\lambda j}(b)=\left(\phi_\lambda(\theta,\phi)\middle|\sum_i\Phi_i(\rho,\phi)S_{ij}(z)\right)_{r=b}\,. \tag{9}$$

In the same way we calculate the derivative $dF_{\lambda j}/dr$ at

$r=b$ and the corresponding irregular function and its derivative [8]. Knowing these four functions from outside $r=b$ and the R matrix $R_{\lambda\lambda'}$ from inside we can calculate the K matrix in (8), and hence the S matrix, in the usual way by equating the two R matrices. Knowing the K matrix and the dipole matrix elements for a given transition, one can calculate the photoionization cross section.

The photoionization cross section can be written in a very compact form related to the field-free cross section. For example, for the s-to-p-type transitions considered here for the alkalis, the cross section is

$$\sigma_B = 4\pi^2\omega\alpha|\langle\psi_\varepsilon^-|\mathbf{r}_m|\psi_0\rangle|^2 = |A_{l=1}^-|^2\sigma_{B=0}. \qquad (10)$$

The minus indicates that the wave function has been transformed from K-matrix to S-matrix normalization. α is the fine-structure constant and ω is the photon frequency. This factorization arises because the field-free $B=0$ wave function only differs from the field-dependent wave function in the region $0 \le r \le a$, where the dipole matrix elements are evaluated, through the constants A in (4). These constants are obtained directly from the matching. (For more general transitions this formula can be related to the trace of a density-of-states matrix [9] as in the Stark effect [10].)

We show in Fig. 1 a sample of the calculated photoionization cross section for lithium in a field $B=6.1143$ T, the field used in recent experimental and theoretical work [2,4], in the energy region just above the ionization threshold but below the first excited Landau level. The spectrum was first calculated over a coarse mesh of energies. (The calculation of the cross section at each such energy took 20 s on a Cray-XMP computer.) Standard semianalytic multichannel quantum-defect methods were then used to calculate the spectrum over the arbitrarily fine mesh of energies shown in Fig. 1 [5]. The radii used were $a=200$, the matching radius $b=7500$, $c=7350$, and the asymptotic radius $d=12000$ a.u. 100 channels or l values were used in (5) and no large matrix diagonalizations were required since the R matrix was propagated from a to b [7]. The inclusion of the first-order coupling term in (3) allowed us to reduce the matching radius to $b=7500$. This could be lowered further by including more terms in (2). Seven to ten Landau channels were retained in the expansion (7). One major advantage of the R-matrix method used here is that one only needs to calculate the eigensolutions in (5) once and then one can calculate the spectrum for *any* atom or molecule with little further computation. One just uses the appropriate quantum defects and R matrix at $r=a$ for the system in question. The only quantities neglected in the present work are the very small remaining long-range potential couplings between Landau states, due to the full potential in (2), which are present in the region $12000 \le z < \infty$. These couplings will result in small perturbations to the spectrum shown in Figs. 1 and 2.

Most of the resonance structure in Fig. 1 is simply due to perturbed Coulomb Rydberg states converging to one of the first few Landau thresholds. To see this more clearly we can calculate the Gailitis average of the spectrum converging to the nearest Landau threshold (the first excited level), i.e., we average the cross section over resonances converging to this threshold [5]. The result is shown in Fig. 2(a) and the spectrum agrees very well

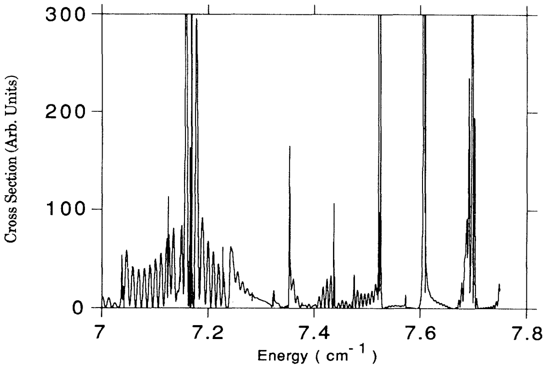

FIG. 1. The photoionization cross section (arbitrary units) from the 3s state of lithium to the $m=0$, odd-parity final states in a field of 6.1143 T as a function of energy in cm^{-1} between the ionization threshold and the first excited Landau level. The energy is measured relative to the field-free ionization threshold.

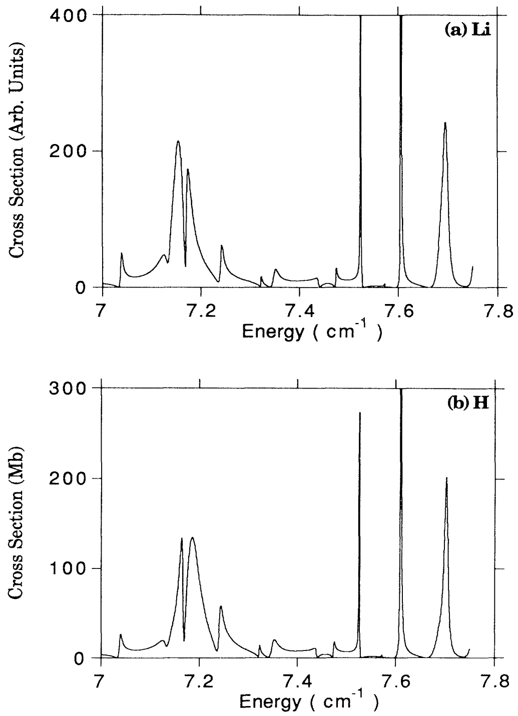

FIG. 2. (a) The spectrum in Fig. 1 averaged over resonances converging to the first excited Landau level (Gailitis average). (b) Same as in (a) for excitation of hydrogen from the 3s level.

with previous calculations and experiment [2,4]. Most of the resonance structure disappears. Clearly the spectrum calculated by the complex coordinate method [4] gives an approximate Gailitis averaged cross section as the theory has inherent difficulties near thresholds. The experiment shows some evidence of the further resonance structure shown in Fig. 1 but it may be that these very weakly bound states are field ionized by stray electric fields. We also show the spectrum for hydrogen. The two spectra are very similar. The small quantum defect $\mu_p = 0.05$ for lithium causes some variations in the relative strength of the resonances as well as a small shift in their positions to lower energies.

The bound-state spectrum in the vicinity of the ionization threshold has also been calculated using the above continuum theory combined with quantum-defect theory, and will be presented elsewhere together with a more extensive analysis of the photoionization spectrum [9]. The bound-state resonances seen in the experiment [2] but unresolved in the complex coordinate method [4] are, as above, due to Rydberg states converging to the ionization threshold. The present continuum theory allows one to reproduce previous [11] bound-state calculations for nonhydrogenic systems [9].

In summary, the present theory has been used to calculate the photoionization cross section for hydrogen and lithium in a laboratory strength field. The formalism is completely general and can be applied to any atom or molecule in an arbitrary strength magnetic field. Much of the resonance structure in the continuum can be understood in terms of complex perturbed Rydberg series.

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