Adiabatic-Expansion Method Applied to Diamagnetic Rydberg Atoms

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We report on a successful implementation of the diabatic-by-sector method as applied to the computation of positive-energy diamagnetic Rydberg spectra of the alkali-metal atoms in a laboratory field (~ 6 T). The method provides the quantum-defect parameters directly, and opens up the possibility of accounting for various spectral features quantum mechanically.

The recent surge of studies [1] on the diamagnetic Rydberg atom is motivated by an intricate connection between the chaotic classical motion [2] and detailed experimental quantum spectra [3]. Two major theoretical objectives that challenge us here are (1) to seek a reliable and efficient scheme capable of reproducing the details of the experimental spectrum of an *arbitrary* atom at both negative and positive energies, and (2) to interpret the spectrum quantum mechanically, and, if possible, to make a quantum-classical correspondence. This Letter presents a scheme that fulfills the first objective. The second one will be dealt with elsewhere.

A brief overview of previous theoretical schemes should help understand the scope of the present work. Roughly speaking, the schemes fall into one of two categories: (i) differential equation approach, and (ii) Hamiltonian matrix approach. A main merit of the former approach is that the concept of continua is built into it in a most natural way. The close-coupling method [4] is a good example. The configuration interaction method [5], on the other hand, is an example of the latter. The recent successful implementation of the complex coordinate method of Delande, Bommier, and Gay [6] is an extension of the Hamiltonian matrix approach; their method mocks up the continua by introducing an imaginary part to the Hamiltonian.

Whichever approach is employed, computing the spectrum of the diamagnetic Rydberg atom at a laboratory field requires technical innovations for achieving numerical stability and efficiency because the extension of the space covered by the system is enormous, being of the order of 10000 a.u. This Letter presents a method that overcomes the difficulties of the differential equation approach.

Let us enlist some essential ingredients of the method [7]: (i) Adiabatic channel functions as a basis set for setting up the close-coupling equation [Eqs. (2) and (4)]; (ii) local frame transformation [Eq. (5)]; (iii) the two-dimensional matching to determine the asymptotically correct S matrix [Eqs. (8)–(10)]; (iv) the multichannel quantum-defect theory (MQDT [8] hereafter) for computing cross sections with an *arbitrarily fine energy mesh*. Let us outline these ingredients. First, the Hamiltoni-

an reads (atomic units)

$$H = -\frac{1}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l^2}{2mr^2} + v(r) + \frac{\beta l_z}{m} + \frac{\beta^2}{2m}(r\sin\theta)^2,$$

(1)

where m is the reduced mass of the electron and $\beta = B/2B_c = 2.13 \times 10^{-4} B$ with the magnetic field B in T. Here $v(r)$ represents the interaction potential of the electron with the residual ion. The adiabatic channel functions are the eigenfunctions of the equation

$$H_{ad}(r,\theta)\phi_i(r;\theta) = U_i(r)\phi_i(r;\theta) \quad (i=1,2,\ldots,\infty),$$

(2)

where

$$H_{ad}(r,\theta) = \frac{l^2}{2mr^2} + v(r) + \frac{\beta l_z}{m} + \frac{\beta^2}{2m}(r\sin\theta)^2.$$

Evaluation of U_i and ϕ_i is most conveniently achieved by diagonalizing H_{ad} in the base of the spherical harmonics. The matrix is tridiagonal and can be rapidly diagonalized. Values sufficiently accurate for our purposes are obtained up to $r \approx 12000$ a.u. with at most 500 basis functions. In the neighborhood of some radial distance r_a ($r_a - \Delta r < r_a < r_a + \Delta r$), the full wave function $\Phi(r,\theta)$ is expanded as

$$\Phi(r,\theta) = \sum_{i=1}^{\infty} \frac{1}{r} F_i(r)\phi_i(r_a;\theta).$$

(3)

This expansion is the heart of the present Letter. The radial wave function $F_i(r)$ satisfies the system of coupled ordinary differential equations hereafter referred to as the close-coupling equation,

$$\left[-\frac{1}{2m}\frac{d^2}{dr^2} - E\right]F_i(r) + \sum_{i'} V_{ii'}(r)F_{i'}(r) = 0,$$

(4)

where $V_{ii'}(r) = \langle \phi_i(r_a;\theta)|H_{ad}(r,\theta)|\phi_{i'}(r_a;\theta)\rangle$. Going from one sector around r_a to its neighboring sector around r_b requires the local-frame-transformation matrix

$$U_{ii'}(a \rightarrow b) = \langle \phi_i(r_a;\theta)||\phi_{i'}(r_b;\theta)\rangle,$$

(5)

which is unitary. With this, the solutions of Eq. (4) are easily referenced to the adiabatic channels of the next

sector. The dipole matrix can be transformed similarly. Details will be given elsewhere.

The fingerprint of each atom enters into this formulation through $v(r)$ of Eq. (1). However, one may set up the initial condition for the close-coupling equation (4), using the quantum defect of the atom, a technique also employed in Ref. [9], thus obliterating the need of the effective potential field. Specifically, we set up the initial condition at $r_0 \sim 50$ a.u., namely,

$$F = 1 , \tag{6}$$

$$\left.\frac{dF}{dr}\right|_{r=r_0} = \left.\frac{f' - K_{core}g'}{f - K_{core}g}\right|_{r=r_0} , \tag{7}$$

where K_{core} is the K matrix at zero magnetic field, and f and g are energy-normalized Coulomb functions as defined and discussed in Ref. [8]. For the alkali metals, the K matrix is diagonal in the spherical basis and its elements are given by $\tan\pi\mu$ (see Ref. [10] for the specific values of μ). The dipole matrix is equated to 1 for the p-wave channel but to 0 otherwise as appropriate to the experiment of Ref. [3]. This means that to calculate the absolute cross section, it is necessary to renormalize the computed cross section by the square of the true dipole matrix.

The solution $\Psi(\mathbf{r})$ is then cast into the K-matrix form at the matching radius r_m,

$$\Psi_a(\mathbf{r}) \propto f_a(z)\psi_a(\rho) - \sum_{a'} K_{aa'}^{(0)} g_{a'}(z)\psi_{a'}(\rho) , \tag{8}$$
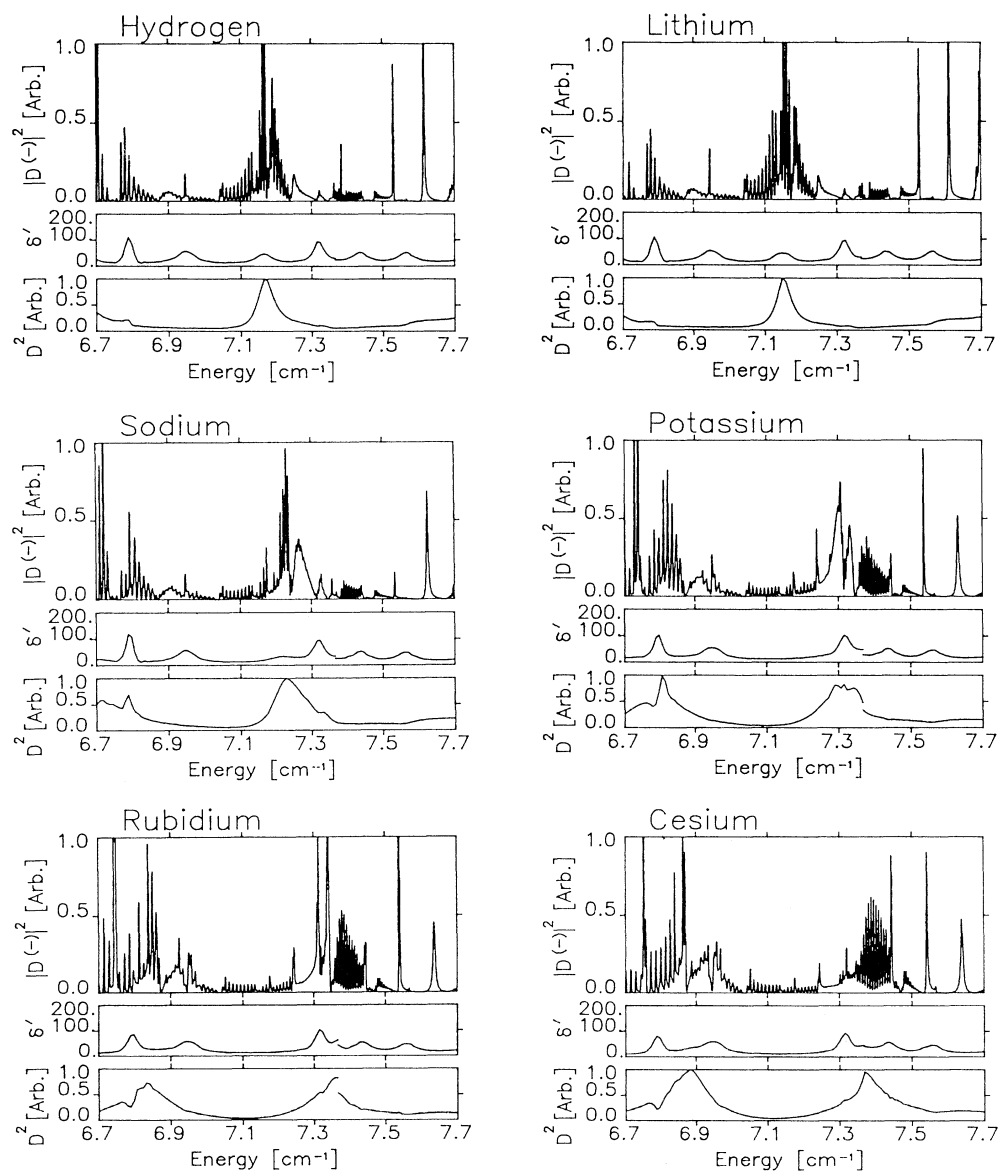

FIG. 1. Master diagram displaying continuum spectra, δ', and D (see text) of alkali-metal atoms (H, Li, Na, K, Rb, Cs).

where

$$f_a(z)\psi_a(\rho) = \sum_i \langle\phi_i(r_m;\theta)||f_a\psi_a\rangle\phi_i(r_m;\theta) \, , \qquad (9)$$

$$g_a(z)\psi_a(\rho) = \sum_i \langle\phi_i(r_m;\theta)||g_a\psi_a\rangle\phi_i(r_m;\theta) \, . \qquad (10)$$

Here f and g are the s-wave Coulomb functions, $\psi_a(\rho)$ is the two-dimensional harmonic-oscillator wave function, the index a pertains to the asymptotic channels and its range coincides with the number of adiabatic channels used in propagating the solutions from small distances, and importantly the integral is along the arc $z^2+\rho^2=r_m^2$. This *two-dimensional matching* yields the asymptotically correct K matrix. The dipole matrix calculated in the spherical coordinates can be similarly transformed into the cylindrical representation. The two-dimensional matching thus executed, the MQDT procedure applies [11]. The dipole matrix $D^{(-)}$ corresponding to the incoming wave is readily deduced. The photoionization cross section is then

$$\sigma = (4\pi^2e^2\omega/c)|D^{(-)}|^2 \, . \qquad (11)$$

Partial cross sections may be computed in the standard way. This, however, will be difficult for a method which dispenses with channels.

The major difficulty associated with the procedure is with generating accurate negative-energy Coulomb functions efficiently at distances of order 10000 a.u. We have solved this by the use of continued fractions as discussed in Ref. [12].

In what follows, numerical integration of the close-coupling equation is performed for the energy range between 6.7 and 7.7 cm^{-1} above the zero-field ionization limit. We included the 33 lowest channels as these are open or weakly closed in some range of r between 0 and $r_m \simeq 12000$ a.u. At the matching radius, about 5 channels are locally open. The K matrix referenced to these locally open channels is constructed and the corresponding eigenphase shifts (δ_a) and dipole matrix (D_a) are evaluated on a coarse mesh. Figure 1 is a master diagram exhibiting the energy derivative of the eigenphase sum $[\delta' = (d/d\epsilon)\sum_a \delta_a]$, and the sum of the square of the eigenchannel dipole matrix $(D^2 = \sum_a |D_a|^2)$. The resulting photoionization cross section, Gaussian convoluted with linewidth $= 0.001$ cm^{-1}, is displayed for each atom at the top of the frame. The details of Rydberg states are smoothed out but their trace remains as rugged features. This diagram enables us to see how sensitively the electronic interaction of the closed-shell core affects the resonance profiles. The finest Rydberg features are certainly influenced strongly. But we call attention to the way each diffuse interloper-type resonance [13] is affected. The interloper-type resonances manifest themselves as peaks in δ'. The features of an interloper become mingled with Rydberg states of the locally open channels, giving rise to the excessively complicated features. Meanwhile the progression of the interlopers shows regu-

larity as indicated by the movement of each peak in δ'. Particularly noteworthy is the fact that those interlopers sensitive to the p-wave quantum defect have large dipole moments, namely, a large value of D. They dictate the major spectral structures except for some sharp peaks attributed earlier to constructive interference known as stabilization [3]. (It turns out that such peaks are members of a Rydberg series with particular values of q, Fano's profile parameter. Indeed, the ultranarrow peak near 6.95 cm^{-1} belongs to the Rydberg series of the second lowest Landau channel just like the three conspicuous peaks near 7.5, 7.6, and 7.7 cm^{-1}.) The following fact may be read off from this tendency. An interloper manifests itself in the dipole matrix D as a hump if its wave function has a moderate amplitude near the nucleus. Its presence is considerably suppressed, however, if its wave function has little overlap with the nucleus. Let us note in passing that the Li and H spectra differ very little. Nonetheless, differences in relative heights of the peaks are rather noticeable, such as the split peaks near 7.15 cm^{-1}.

Figure 2 compares our result for Li with an experimental one [3]. There appears to be a systematic relative energy shift of about 8×10^{-3} cm^{-1} in spite of the suggested correspondence between experimental and theoretical magnetic-field strengths. The overall agreement is nevertheless excellent. Note that on account of the interaction of the Rydberg states with one continuum the unconvoluted cross section goes to zero between successive peaks. The profile parameter of each resonance is a good measure of the accuracy of a theoretical scheme, but we forego enlisting the representative values of the parameter until another occasion.
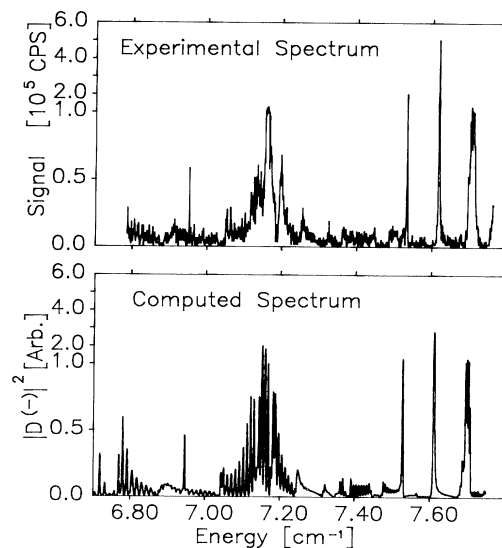

FIG. 2. Comparison of the experimental (above) and theoretical (below) spectra of lithium in the continuum region. (Experimental data by courtesy of Kleppner and Iu.)
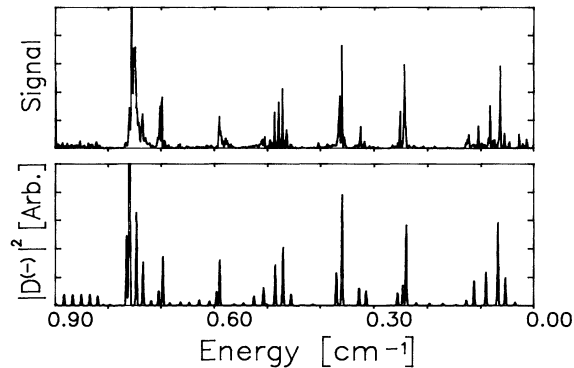
FIG. 3. Comparison as in Fig. 2 for bound states. (Experimental spectrum by courtesy of Kleppner and Iu and theoretical spectrum by courtesy of Koshino.)

The method applies to negative energies equally well. We display in Fig. 3 the convoluted absorption spectrum in the range 0.0–0.9 cm^{-1} calculated at $B = 6.092$ T, together with the experimental one [3] at $B = 6.0898$ T. The theoretical spectrum of Ref. [6] misses the closely spaced bound states. Instead their method provides a band profile whose width appears to stem from that of an interloper state. The experimental density of states appears as roughly twice the theoretical one, suggesting an involvement of some stray electric field causing the Stark mixing of even- and odd-parity states [14].

Experiments on various atoms with an improved resolution and efforts to sift out the effect of stray fields from experimental spectra should stimulate further theoretical studies.

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