

LETTER TO THE EDITOR

**The combination of  $R$ -matrix and complex coordinate methods: application to resonances in the diamagnetic Rydberg spectrum of Li**

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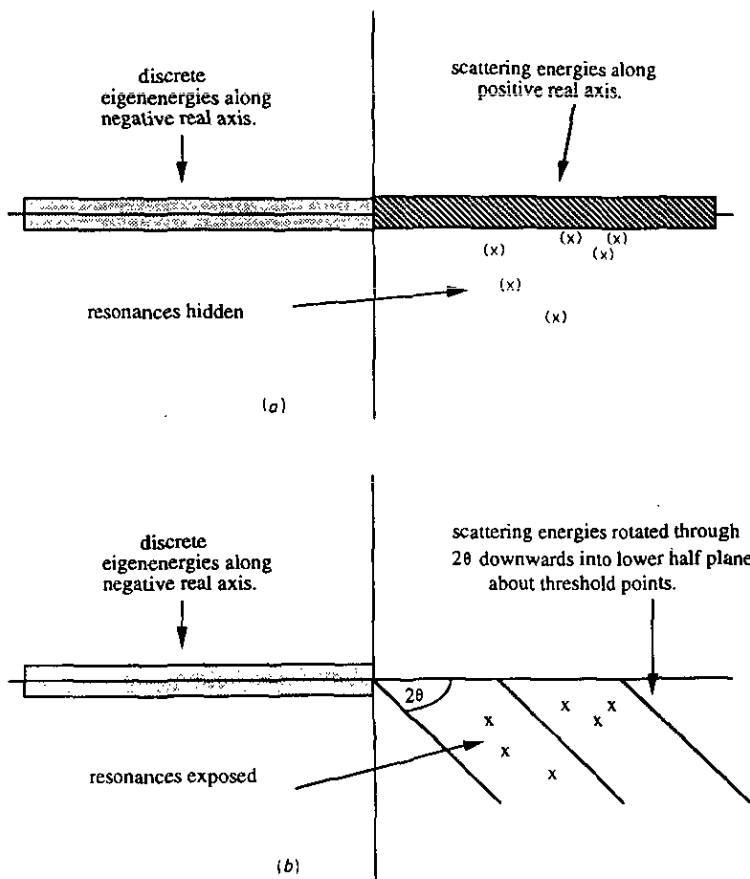
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**Abstract.** The  $R$ -matrix and complex coordinate techniques are combined for the first time and applied to the problem of the positive energy spectrum of a non-hydrogenic atom in a laboratory strength magnetic field. Quantum defect theory is extended to calculate the appropriate irregular Coulomb function at complex energy and complex radial distance. Calculations are carried out for lithium to compare with recent experimental measurements and with a corresponding calculation for hydrogen.

In this letter we report the development of, and first results obtained from, a new computational approach that, for the first time, brings together the complex coordinate rotation method (Delande *et al* 1991), and the  $R$ -matrix method (Burke *et al* 1971). We describe briefly the fundamental concepts of these two methods before addressing specifically the application of the combination to the calculation of the above threshold spectrum of the lithium atom in a magnetic field—the subject of recent high resolution experiments (Iu *et al* 1989, 1991). We discuss an important extension of our basic idea which has made this application computationally feasible. The new method has also demanded knowledge of regular and irregular Coulomb functions, for both complex energy and complex radial distance, and the consequently unavoidable new work needed to formulate the irregular function of quantum defect theory in this situation is briefly outlined. Full details on all these developments are reserved for a full-scale paper, but we illustrate the precision of our calculations by comparing results obtained for lithium with the experimental data and with those from a recent complex coordinate calculation for hydrogen (Delande *et al* 1991).

The complex rotation method hinges on the rotation of the radial variable  $r$  into the complex plane. We use the notation  $r \rightarrow r e^{i\theta}$  where  $\theta$  is the rotation angle. Similarly, the radial momentum  $p$  is rotated in the other direction  $p \rightarrow p e^{-i\theta}$  which preserves canonical commutation relations. When all operators are scaled in this way, the Hamiltonian  $H$  is transformed to a new rotated Hamiltonian  $H(\theta)$ —a non-Hermitian operator whose spectrum is complex. In addition, if represented over a real basis of functions,  $H(\theta)$  is a complex symmetric operator. The power of the complex rotation technique comes from the fact that the spectrum of  $H(\theta)$  is

related to the one of  $H$  as follows: the discrete states of  $H$  are still real eigenvalues of  $H(\theta)$ ; the continua of  $H$  are rotated in the complex plane by an angle  $-\theta$  and the additional isolated eigenvalues of  $H(\theta)$  are the resonances of  $H$  (i.e. poles of the analytic continuation of  $1/(H - E)$  in the lower half-plane). These normally hidden resonances are revealed by the complex rotation. The effect of the rotation on the energy eigenvalues of a typical problem is shown in figure 1. Thus a simple diagonalization of the non-Hermitian, but, with real basis functions, complex symmetric  $H(\theta)$  operator gives a complete description of both the discrete and continuum spectrum of the Hamiltonian  $H$ , including positions, widths and shapes of resonances.



**Figure 1.** Schematic diagram showing change in eigenenergy spectrum of an atomic system brought about by a complex coordinate rotation: (a) without complex rotation, (b) with complex rotation.

In  $R$ -matrix theory (Burke *et al* 1971), configuration space is divided into two regions and a different method of solution can be used in each. This is most advantageous when the Hamiltonian for the system has a distinctly different form in each of the regions. For the problem of a non-hydrogenic system in a magnetic field, the one-electron Hamiltonian  $H$  in the outer region is, in atomic units,

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{1}{8}\gamma^2(x^2 + y^2) \quad a \leq r \leq \infty \quad (1)$$

with  $\gamma = B/B_0$  where  $B$  is the strength in tesla of the magnetic field directed along the  $z$ -axis and  $B_0 = 2.35 \times 10^5$  T. (The only good quantum numbers are  $m$  and parity with the consequence that the linear Zeeman term  $\gamma l_z/2$  is a constant of the motion and is omitted.) An  $R$ -matrix can be formed on the inner boundary  $r = a$  of this region as follows (Monteiro and Taylor 1990): the Hamiltonian in (1), augmented by surface terms constructed at  $r = a$ , to make it Hermitian over this limited region (Bloch 1957), is first diagonalized in a basis of spherical functions each characterized by an angular momentum  $l$ . Then from knowledge of *all* the eigenvalues and corresponding eigenvectors we have for an  $R$ -matrix at energy  $E$ ,

$$R_{l,l'}(a, E) = \sum_k \frac{u_l^k(a) u_{l'}^k(a)}{E - E_k} \quad (2)$$

where  $E_k$  is the  $k$ th eigenvalue and  $u_l^k(a)$  is the value on the boundary of the  $k$ th outer region eigenfunction with angular momentum  $l$ .

On the other hand, in the inner region, the diamagnetic term can be neglected (provided  $\gamma^2 a^2$  is sufficiently small) and the complicated multi-electron dynamics is the same as in the absence of a magnetic field. It can be usefully accounted for by writing the reduced radial function of each angular momentum  $l$  at  $r = a$  and at energy  $E$  as

$$U_l(a) = a_l \{s_l(a) + \tan(\pi\mu_l)c_l(a)\} \quad (3)$$

where  $s_l$  and  $c_l$  are energy normalized regular and irregular Coulomb functions respectively, and  $\mu_l$  is the (energy dependent, but field independent) quantum defect for angular momentum  $l$ —possibly taken from experiment. The eigenenergy  $E$  of the complete problem together with the coefficients  $a_l$  are determined by requiring the matching condition

$$\mathbf{U}(a) = \mathbf{R}(a, E) \left. \frac{d\mathbf{U}(r)}{dr} \right|_{r=a} \quad (4)$$

to be satisfied where  $\mathbf{U}$  is the diagonal matrix with  $U_l(a)$  as elements.

We combine the methods by applying the  $R$ -matrix procedure outlined above to the complex rotated problem. Thus in the outer region, the Hamiltonian (1) is subjected to a complex rotation of its radial variables, and, augmented by surface terms constructed at the complex radial distance  $ae^{i\theta}$  (to make it a *complex symmetric* operator over this limited region) is diagonalized in the same basis as before. An expression analogous to equation (2) but in which every quantity appearing is complex, now defines a complex  $R$ -matrix at the complex energy  $E$ . Similarly to before for the inner region, phase shifted Coulomb functions for each angular momentum  $l$ , but now for complex energy, must be formed at the complex boundary  $ae^{i\theta}$  and the matching energy and coefficients found through satisfying an equation analogous to (4). These matching energies are found by performing an energy search which in this case must be carried out over the two-dimensional complex energy plane. Finding all eigenvalues and eigenvectors of the outer region complex rotated Hamiltonian—with dimension of  $\sim 60\,000$  in the near-threshold energy region of interest—is difficult, as is a two-dimensional energy search in the near-threshold region where there is a very high density of energy levels. Instead we have extended our method to take advantage

of an idea first put forward by Schneider (1981) and which we now take over into the complex rotated problem. This idea allows information about the inner region solution at energy  $E$  and at the complex matching radius  $ae^{i\theta}$  to be built in *before* diagonalization is carried out over the outer region. When subsequently performed, the outer region diagonalization then yields an eigenvalue at the eigenenergy  $E$  of the complete problem and a corresponding eigenfunction over the outer region which coincides also, over this region, with the eigenfunction of the complete problem. The inclusion of inner region information is achieved by adding further surface terms  $B_l$  to the diagonal terms of the Hamiltonian matrix over the outer region. In the complex rotated case we find these take the form

$$B_l = \frac{e^{i\theta}}{U_l(ae^{i\theta})} \left. \frac{dU_l(re^{i\theta})}{dr} \right|_{r=a} \quad (5)$$

where  $U_l(ae^{i\theta})$  is the complex rotated form of the function in equation (3). Since the eigenenergy  $E$  is not known precisely, in advance of the diagonalization, this, in practice, is a viable procedure if the  $B_l$  vary little with energy over the spectral range of interest. The overwhelming advantage, compared to conventional  $R$ -matrix work, is that one needs to find from the outer region diagonalization only as many eigenvalues and eigenfunctions as are eigenvalues and eigenfunctions for the complete problem. This can be typically 100 from a matrix of order 60 000. We thus diagonalize the adjusted outer region Hamiltonian over a basis of real Sturmian functions  $S_{nl}^{(\zeta)}(r)$ —which are particularly suitable for handling the quadratic Zeeman Hamiltonian (Clark and Taylor 1982)—so that we write the reduced radial portion of the angular momentum  $l$  component of an eigenfunction resulting from diagonalization as

$$U_l(re^{i\theta}) = \sum_n c_{nl}(\theta) S_{nl}^{(\zeta)}(r) \quad (6)$$

where the  $c_{nl}(\theta)$  are complex coefficients. Alternatively, we have

$$\mathbf{H}\mathbf{x} = E\mathbf{B}\mathbf{x} \quad (7)$$

where the overlap matrix  $\mathbf{B}$  occurs because of the non-orthogonality of the Sturmian basis. The eigenvector  $\mathbf{x}$  comprises the coefficients  $c_{nl}(\theta)$  pertaining to energy eigenvalue  $E$ . Both matrices in (7) are banded and the Hamiltonian  $\mathbf{H}$ -matrix has a block structure due to coupling of adjacent same-parity  $l$  by the magnetic field. The detailed structure of the matrices is given by the properties of the Sturmian functions, whose selection rules with  $n$  are lost since all the radial integrals are taken over the range  $a \leq r \leq \infty$ . We find that even more of the eigenvalues (and corresponding eigenfunctions) from equation (7) coincide with those of the complete problem if the  $B_l$  terms are allowed to have a linear energy dependence. This, in fact, approximates very well their actual behaviour away from singularities. This does not present any additional computational difficulties since we have a generalized energy eigenvalue problem in equation (7) to handle in any case. The diagonalization is performed using a version of the shifted Lanczos method appropriate to complex banded symmetric matrices written originally for the work on diamagnetic hydrogen by Delande *et al* (1991).

The Coulomb functions coming into the  $B_l$  of equation (5) must be evaluated at complex energy and for complex radial coordinate. To do this we extend the quantum defect theory of Coulomb functions into the complex radial distance and energy planes. Following Seaton (1983) we use  $Z$ -scaled atomic units for all quantities except energy  $\epsilon$  for which we use  $Z$ -scaled Rydbergs where  $Z$  is the nuclear charge. As indicated schematically in figure 1 we are interested in complex energies in the lower half-plane. In order to have continuity as the negative real axis is approached from below, we define:

$$\rho = re^{i\theta} \quad \text{for } 0 \leq \theta \leq \pi/2 \tag{8}$$

$$\epsilon = |\epsilon|e^{i\varphi} \quad \text{for } -\pi \leq \varphi \leq 0 \tag{9}$$

$$\kappa = \sqrt{-\frac{1}{\epsilon}} = |\kappa| \exp \left[ -i \left( \frac{\pi}{2} + \frac{\varphi}{2} \right) \right] \tag{10}$$

$$z = \frac{2\rho}{\kappa} = \frac{2r}{|\kappa|} \exp \left[ i \left( \theta + \frac{\varphi}{2} + \frac{\pi}{2} \right) \right] \tag{11}$$

$$f(\kappa, l; z) = \kappa^{l+1} \exp(-i\pi\kappa) \left( \frac{\exp[i\pi(l+1)]W_{\kappa, l+1/2}(z)}{\Gamma(\kappa+l+1)} + \frac{W_{-\kappa, l+1/2}[z \exp(-i\pi)]}{\Gamma(-\kappa+l+1)} \right) \tag{12}$$

where  $W$  is the Whittaker function,  $f$  is the regular Coulomb function and these definitions mean that  $z$  has always a positive argument.

The irregular Coulomb function of quantum defect theory (Seaton 1983), must lag the regular one in phase by  $\pi/2$ . For the case of real energy and real radial coordinate, it was possible to impose this lag asymptotically for positive energies and to continue the definition across  $\epsilon=0$  for negative energies. This cannot be done in the complex case as, in general, the regular function is exponentially increasing. We impose the phase lag in some intermediate region and consider the case of small energies: we find that in the region of  $|\epsilon| = 0$ ,

$$h(\kappa, l; z) = \kappa^{l+1} \exp(-i\pi\kappa) \left( i \frac{(-1)^{l+1}W_{\kappa, l+1/2}(z)}{\Gamma(\kappa+l+1)} - \cot(\pi\kappa) \frac{W_{-\kappa, l+1/2}(z \exp[-i\pi])}{\Gamma(-\kappa+l+1)} \right). \tag{13}$$

We can then define the appropriate energy normalized Coulomb functions  $s$  and  $c$  by

$$s = \sqrt{\frac{B}{2}} f \quad \text{and} \quad c = \sqrt{\frac{1}{2B}} h \tag{14}$$

where

$$B(\epsilon, l) = A(\epsilon, l) + \text{Im} \left[ \frac{A(\epsilon, l)}{2\pi} \{ \psi(\kappa+l+1) + \psi(\kappa-l) - 2 \ln(\kappa) \} \right] \tag{15}$$

and

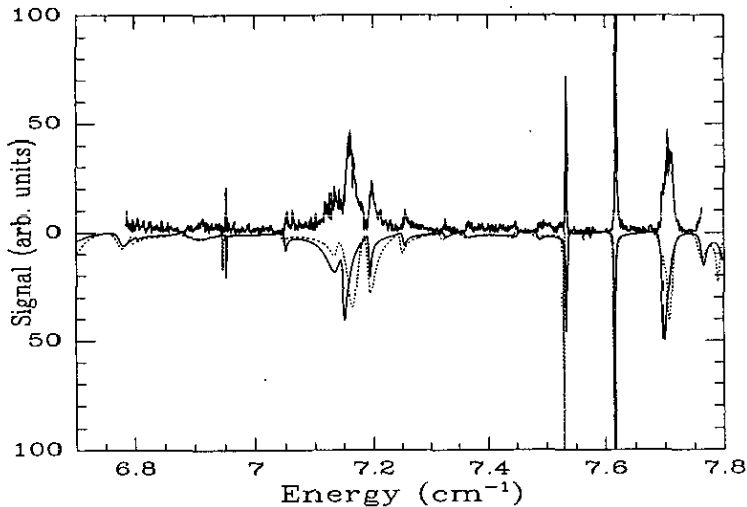
$$A(\epsilon, l) = \frac{\Gamma(\kappa + l + 1)}{\kappa^{2l+1}\Gamma(\kappa - l)} = \prod_{p=0}^l (1 + p^2\epsilon). \quad (16)$$

Following Delande *et al* (1991) the photoionization cross section  $\sigma(\omega)$  from some initial state  $|\psi_0\rangle$  with energy  $E_0$  is given by

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \langle \psi_0 | T \frac{1}{H - \omega - E_0 - i\epsilon} T | \psi_0 \rangle \quad (17)$$

where  $T = e \cdot r$  is the dipole operator for polarization  $e$ . Introducing the complex rotation and writing  $|\psi\rangle$  as the complex-rotation transform of  $T|\psi_0\rangle$ , which we expand as  $|\psi\rangle = \sum c_i(\theta) |\phi_i(\theta)\rangle$  where  $|\phi_i(\theta)\rangle$  are the eigenvectors of  $H(\theta)$ , we have finally

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \sum_i \frac{c_i^2(\theta)}{E_i(\theta) - \omega - E_0}. \quad (18)$$



**Figure 2.** Comparison of an above-threshold experimental spectrum for lithium (above) with the calculated spectrum (full line below) and the calculated spectrum for hydrogen (broken line). The experimental spectrum was obtained by photoionizing the 3s state of lithium in a measured magnetic field of  $6.1131 \pm 0.001$  T whilst the calculations were carried out for photoionization of the same state in a field of 6.1143 T and convoluting the cross section with a Gaussian window with  $1 \times 10^{-3}$   $\text{cm}^{-1}$  linewidth, equal to the experimental resolution.

In figure 2 we compare our calculated results for the spectrum of lithium over an energy range of  $6.7 \text{ cm}^{-1}$  to  $7.8 \text{ cm}^{-1}$  above the field-free ionization threshold, with the experimental results and the previously calculated results for hydrogen obtained by Iu *et al* (1991) using the complex coordinate approach. Both calculated spectra correspond to photoionization out of the 3s state of the atom to an  $m = 0$  odd-parity

final state in a magnetic field strength of 6.1143 T and in each case the calculated cross section was convoluted with a Gaussian profile with the experimental linewidth,  $1 \times 10^{-3} \text{ cm}^{-1}$ . Our lithium computation involved 62 500 basis functions and used 1.586 Gbytes of memory for a little over 40 minutes on a Convex C3 computer at the University of London Computer Centre.

We note that in our calculated results for lithium: (i) the absolute values of experimental and theoretical energies are in almost perfect agreement—the order of magnitude of discrepancy is  $10^{-3} \text{ cm}^{-1}$  which is within the experimental accuracy. This is in contrast with the hydrogen spectrum computed by Iu *et al* (1991) where it was necessary to shift the spectrum by  $3 \times 10^{-3} \text{ cm}^{-1}$  in order to obtain best agreement, and where the discrepancy was of the order of  $3 \times 10^{-3} \text{ cm}^{-1}$ ; (ii) there is a more accurate representation of the peaks around  $7.15 \text{ cm}^{-1}$  than obtained in the hydrogen calculation, especially for the intensities of the lines; (iii) some peaks are shifted to *higher* energies (as compared to hydrogen) whilst others are shifted downwards in energy.

Using the diabatic-by-sector method of Launay and Le Dourneuf (1982), the spectrum over this energy range has also been calculated for hydrogen and *all* the alkalis by Watanabe and Komine (1991) and for hydrogen and lithium by O'Mahony and Mota-Furtado (1991). Although the different spectra for lithium are in fair agreement with the experiment and one with the other, some differences are visible. In the present calculation, the small oscillations in the cross section due to extremely high lying Rydberg states converging to the second Landau threshold are not reproduced because the basis size is too small. However, these oscillations are not very important and are not seen in the experimental spectrum, probably because they are smoothed out by a stray electric field. On the other hand, the two spectra obtained by the diabatic-by-sector method should be identical, which is not the case and suggests that at least one of them is not fully converged.

Both the diabatic-by-sector and complex coordinate plus *R*-matrix methods can yield accurate results at laboratory field strengths, with roughly the same computer effort. The diabatic-by-sector method has the advantage of being able to reproduce the small oscillations discussed above, because it uses the known asymptotic forms of the wavefunctions. On the other hand, it requires the problem to be solved on a grid of energy values and ultra-narrow resonances as observed by Iu *et al* (1989) can be missed. The method used in this letter is free of this disadvantage and generates the full spectrum in a single diagonalization. Furthermore, in more complex situations (for example, in crossed electric and magnetic fields) where no asymptotic solution is known in the laboratory frame, it is the only presently available method.

Work is continuing on further developments and applications of the new method presented here and these will be reported in due course as will a full description of the new theory outlined above.

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