Study of the photoabsorption spectrum of diamagnetic Rydberg atoms without the need of using full eigenvectors

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We present a new method for efficient and accurate determination of the eigenvalues and the photoabsorption spectrum of Rydberg atoms in the presence of uniform magnetic fields. The procedure consists of the following elements: (a) Hamiltonian and basis set based on the SO(4, 2) dynamical group and its SO(2, 1) subgroup; (b) Lanczos algorithm with spectrum transformation for dealing with the "internal" energy spectrum of ultralarge sparse symmetric Hamiltonians; and (c) a new procedure for the calculation of photoabsorption spectra of Rydberg atoms without the need of determining and using the full eigenvectors of very large dimension. The method is applied to the photoabsorption spectrum of diamagnetic Rydberg hydrogen atoms in the energy regime close to the ionization threshold where the corresponding classical behavior is chaotic. Good agreement with experimental data is obtained.

1. Introduction

During the last several years, a great deal of new interest has been paid to the study of the physics of diamagnetic Rydberg atoms. A number of experiments [1-3] and theoretical calculations (see, c.g., the recent reviews of ref. [4]) [5,6] have been performed on Rydberg states near the field-free ionization threshold. This is a fundamental problem of general importance with implications well beyond atomic physics. As one approaches the ionization limit, the system shows a transition from regularity to irregularity which is manifest both in the classical trajectories and in the corresponding quantum level distributions [4]. As such, the diamagnetic Rydberg H atom provides one of the very few real systems for which one can study the quantum manifestations of classical chaos both experimentally and theoretically.

The difficulty associated with the study of the motion of the Rydberg electron in a magnetic field stems from the competition between two potentials of different symmetry (namely, spherical symmetry in the Coulomb field and cylindrical symmetry in the magnetic field) and the nonseparability of the Schrödinger equation. In this Letter, we present a new method for efficient and accurate determination of the photoabsorption spectrum of diamagnetic Rydberg atoms in the regime where the corresponding classical behavior is chaotic.

2. Dynamical SO(4, 2) group for diamagnetic hydrogen atom

The Hamiltonian of atomic hydrogen in a magnetic field (along the z axis) is given by (in atomic units)

\[ H = \frac{1}{2} p^2 - 1/r + \frac{1}{2} \gamma l_z + \frac{1}{2} \gamma^2 (x^2 + y^2), \]

where \( l_z \) is the z component of the angular momentum, is a constant of motion \( (\mu=m) \), and \( \gamma = B/B_0 \) \( (B_0 = 2.35 \times 10^5 \ T) \). In the semiparabolic coordinates \( (\mu, \nu, \phi) \), where

\[ \mu = (r+z)^{1/2}, \quad \nu = (r-z)^{1/2}, \]
\[ \tan \phi = y/x, \]

the Hamiltonian, eq. (1), reduces to the following generalized eigenvalue problem [7]:

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\[
\left[\frac{1}{2}\left(-\frac{1}{\mu}\frac{\partial}{\partial \mu} + \frac{m^2}{\mu^2} - \frac{1}{\nu}\frac{\partial}{\partial \nu} + \frac{m^2}{\nu^2}\right) - 2 \frac{1}{2}y^2\mu^2\nu^2(\mu^2 + \nu^2)\right] \Psi(\mu, \nu) = (E - \frac{1}{2}ym)(\mu^2 + \nu^2) \Psi(\mu, \nu).
\]

For the unperturbed atomic hydrogen \((\gamma = 0)\), the Coulomb problem is represented by a pair of uncoupled two-dimensional harmonic oscillators with the same angular momentum \(m\) and frequency \(\omega = 1\).

The symmetric structure of two 2D oscillators suggests the use of the boson operators to build the \(SO(4, 2)\) group [8] with fifteen generators [6,7]. The dynamical group \(SO(4, 2)\) has a rich subgroup structure. It can be shown that the non-invariance algebra associated with eq. (3) is the direct product \(SO(2, 1) \otimes SO(2, 1)\). The generators of the first (second) subgroup \(SO(2, 1)\) can be realized in terms of the \(\mu\) coordinate as follows [7]:

\[
S_x = \frac{1}{4} \left( \pm \frac{\partial^2}{\partial \mu^2} \pm \frac{\partial}{\partial \mu} \mp \frac{m^2}{\mu^2} + \mu^2 \right),
\]

\[
S_y = \frac{1}{2} \left(1 + \mu \frac{\partial}{\partial \mu}\right),
\]

(4a)

and

\[
T_x = \frac{1}{4} \left( \pm \frac{\partial^2}{\partial \nu^2} \pm \frac{\partial}{\partial \nu} \mp \frac{m^2}{\nu^2} + \nu^2 \right),
\]

\[
T_y = \frac{1}{2} \left(1 + \nu \frac{\partial}{\partial \nu}\right).
\]

(4b)

These generators fulfill the \(SO(2, 1)\) commutation relations,

\[
[S_x, S_y] = -iS_z; \quad [S_y, S_z] = iS_x;
\]

\[
[S_z, S_x] = iS_y,
\]

(5a)

and

\[
[T_x, T_y] = -iT_z; \quad [T_y, T_z] = iT_x;
\]

\[
[T_z, T_x] = iT_y.
\]

(5b)

The Casimir operators are

\[
\frac{1}{4}(1 - m^2) = S_x^2 + S_y^2 - S_z^2 = S^2,
\]

\[
T_x^2 + T_y^2 - T_z^2 = T^2.
\]

(6a)

(6b)

In terms of the realization of \(S\) and \(T\), the eigenvalue problem, eq. (3), is now replaced by

\[
[S_z - S_x + T_z - T_x - 2 + \gamma^2(S_x + S_z)(T_x + T_z)(S_x + S_z + T_x + T_z)] \Psi
\]

\[
= 2(E - \frac{1}{2}ym)(S_z + S_x + T_z + T_x) \Psi.
\]

(7)

It is advantageous at this point to introduce a Lorentz rotation generated by \(S_x + T_x\), yielding

\[
\hat{H}\Psi = (E - \frac{1}{2}ym)M\Psi,
\]

(8)

where

\[
\Psi = \exp\left[-i\theta(S_x + T_x)\right]\Psi,
\]

(9a)

\[
\hat{H} = (S_z - S_x + T_z - T_x) e^\theta - 2 + \gamma^2 e^{-3\theta}(S_x + S_z)
\]

\[
\times (T_x + T_z)(S_x + S_z + T_x + T_z),
\]

(9b)

and

\[
M = 2(S_x + S_z + T_z + T_x).
\]

(9c)

The tilt angle \(\theta\) depends on the energy \(E\) and plays an essential role in the current study. In the case of zero magnetic field \((\gamma = 0)\), for example, the eigenvalues \((E < 0)\) and eigenstates of the atomic hydrogen can be obtained by setting

\[
\theta = -\ln n = \frac{1}{2} \ln (-2E),
\]

(10)

where \(n\) is the principal quantum number. The transformation \(\exp\left[-i\theta(S_x + T_x)\right]\) allows the shift of the eigenvalue spectrum, eq. (8), into the region of interest \((E \leq 0)\). Thus the whole spectrum of diamagnetic hydrogen atom can be studied by tuning \(\theta\).

In terms of the eigenstates of \(S_z\), \(S^2\), and \(T_x\), \(T^2\), the basis function appropriate for constructing the matrices \(\hat{H}\) and \(M\) is the associated Laguerre function [9],

\[
|n_1, n_2, m\rangle = 2(-1)^{n_1 + m_1}\frac{n_1!n_2!}{(n_1 + |m|)!(n_2 + |m|)!},
\]

(11)

\[
\times \exp\left[-(\mu^2 + \nu^2) L^{m_1}_{n_1}(\mu^2)L^{m_1}_{n_2}(\nu^2)\right],
\]

where \(n_1\) and \(n_2\) are the parabolic quantum numbers, and \(n = n_1 + n_2 + |m|\). Because the parity \((z \rightarrow -z)\) is conserved, a symmetrization (for even-parity states) or anti-symmetrization (for odd-parity states) of the basis functions is needed. The resultant matrices \(\hat{H}\)
and $M$ are sparse symmetric matrices with band structures (fig. 1). In section 3, we discuss a Lanczos algorithm for the solution of this problem.

3. The Lanczos algorithm with spectrum transformation for large sparse generalized symmetric eigenvalue problems

The Lanczos algorithm is a powerful iteration method for tridiagonalizing a matrix. Much literature [10] has been devoted to the implementation of this algorithm in different physical contexts. However, this algorithm is best only for “extreme” eigenvalues. For the diamagnetic hydrogen atom, we are interested in the “internal” spectrum below and above the ionization threshold. Thus direct application of the Lanczos algorithm to eq. (8) is not appropriate. In the following, we extend a spectrum transformation Lanczos method [11] to the diamagnetic atomic hydrogen problem, allowing the conversion of the “internal” spectrum problem into an “extreme” eigenvalue problem.

For a generalized symmetric eigenvalue problem,

$$\hat{H} |\Psi_i\rangle = E_i \hat{M} |\Psi_i\rangle ,$$  \hspace{1cm} (12)

where $H^T = \hat{H}$ can be real or complex and $\hat{M}^T = \hat{M}$ is positive semidefinite. The spectrum transformation converts eq. (12) into the shifted and inverted form,

$$\left(\frac{1}{\hat{H} - \lambda \hat{M}}\right) \hat{M} |\Psi_i\rangle = \frac{1}{E_i - \lambda} |\Psi_i\rangle ,$$  \hspace{1cm} (13)

where $\lambda$ is a shift in energy. The advantage of eq. (13) is that the extreme eigenvalues of the spectrum now center around the value of $\lambda$. Applying the Lanczos algorithm to eq. (13) will first yield the eigenvalues near $\lambda$. The spectrum of interest, as a result, can be covered by sweeping $\lambda$. The inverse operation $(\hat{H} - \lambda \hat{M})^{-1}$ can be facilitated by using efficient algorithms for LU decompositions of sparse matrices.

To do so, we first use the Cholesky decomposition for $\hat{M}$,

$$\hat{M} = LL^T ,$$  \hspace{1cm} (14)

where $L$ is an upper triangular matrix. Using eq. (14), and setting

$$|\Phi_i\rangle = L^T |\Psi_i\rangle ,$$  \hspace{1cm} (15)

eq. (13) can be reduced to a symmetric ordinary eigenvalue problem.

$$L^T \left(\frac{1}{\hat{H} - \lambda \hat{M}}\right) L |\Phi_i\rangle = \frac{1}{E_i - \lambda} |\Phi_i\rangle .$$  \hspace{1cm} (16)

We can now apply the Lanczos tridiagonalization method to eq. (16). Thus starting from an initial vector $|x_1\rangle$, one can construct the self-energy $\alpha$, and the nearest-neighbor coupling energy $\beta_{i+1}$, iteratively ($i = 1, 2, ..., n$),

$$|w_{i+1}\rangle = \frac{1}{\hat{H} - \lambda \hat{M}} \hat{M} |x_i\rangle - \alpha_i |x_i\rangle - \beta_{i-1} |x_{i-1}\rangle = \beta_i |x_{i+1}\rangle ,$$  \hspace{1cm} (17a)
\[ \alpha_i = \langle x_i | \hat{M} \left( \frac{1}{\hat{H} - \lambda} \right) \hat{M} | x_i \rangle - \beta_i | x_i - 1 \rangle, \]  
\[ \beta_i = \sqrt{\langle w_{i+1} | \hat{M} | w_{i+1} \rangle}, \]  
\[ | x_{i+1} \rangle = \frac{1}{\beta_i} | w_{i+1} \rangle. \]  

For \( n \)-step Lanczos iteration, the \( N \times N \) matrix \( \hat{H} \) is approximated by an \( n \times n \) symmetric tridiagonal matrix:

\[
T_n = \begin{pmatrix}
\alpha_1 & \beta_1 & 0 & \cdots \\
\beta_1 & \alpha_2 & \beta_2 & 0 \\
0 & \beta_2 & \alpha_3 & \beta_3 \\
& \vdots & & \\
& & \beta_{n-1} & \alpha_n
\end{pmatrix}.
\]

In general, \( n \ll N \). Thus the spectrum transform Lanczos method provides a powerful numerical technique for the treatment of the "internal" spectrum of ultralarge sparse generalized symmetric Hamiltonians.

The eigenvalues of the matrix \( T_n \), \( \mu_i \) (\( i = 1, 2, \ldots, n \)), are related to the eigenvalues \( \mu_i \) of eq. (12), by

\[ E_i = 1/\mu_i + \lambda. \]

The corresponding eigenvectors of \( T_n \) will be denoted by the column vectors \( | \phi_i \rangle \). The latter are related to the eigenvectors \( | \Psi_i \rangle \) of \( \hat{H} \), eq. (12), by the following transformation:

\[ | \Psi_i \rangle = \tilde{V} | \phi_i \rangle. \]

Here \( \tilde{V} \) is an \( N \times n \) matrix given by

\[ \tilde{V} = \langle | x_1 \rangle, | x_2 \rangle, | x_3 \rangle, \ldots, | x_n \rangle, \]

where \( | x_i \rangle \) are the \( N \times 1 \) recursive (column) vectors determined from the Lanczos iteration, eq. (17).

\[ f_{0,j} = 2(E_0 - E_j) | \langle \Psi_0 | zM | \Psi_j \rangle |^2, \]

for a generalized eigenvalue problem, eq. (12). Following a similar spirit to the recursive residue generation method [12] (RRGM), we describe below a new procedure for the determination of the oscillator strength, eq. (22), without the need of calculating the \( N \times 1 \) full eigenvectors \( | \Psi_j \rangle \). We choose the initial state of the Lanczos iteration to be

\[ | x_i \rangle = \frac{1}{\sqrt{N_0}} | \Psi_0 \rangle, \]

where \( N_0 \) is the normalization constant with respect to \( M \):

\[ N_0 = \langle \Psi_0 | zMz | \Psi_0 \rangle. \]

The transition amplitude \( \langle \Psi_0 | zM | \Psi_j \rangle \) in eq. (22) is propagated in the Lanczos iteration. Thus,

\[ \langle \Psi_0 | zM | \Psi_j \rangle = \langle \Psi_0 | z\tilde{V} \tilde{V}^\dagger | \phi_j \rangle = \sqrt{N_0} \langle 1 | \tilde{V}^\dagger M \tilde{V} | \phi_j \rangle = \sqrt{N_0} \langle 1 | \phi_j \rangle. \]

where use has been made of eqs. (20), (21), and (23), as well as the equality \( \tilde{V}^\dagger M \tilde{V} = 1 \). Here \( \langle 1 \rangle = (1, 0, 0, \ldots, 0) \) is the "first" unit row vector. Eq. (25) suggests that the transition amplitude \( \langle \Psi_0 | zM | \Psi_j \rangle \) can be determined simply by the first element of the \( n \times 1 \) column eigenvector \( | \phi_j \rangle \), where \( | \phi_j \rangle \) is the \( j \)th eigenvector of \( \tilde{T}_n \),

\[ \tilde{T}_n | \phi_j \rangle = \mu_j | \phi_j \rangle. \]

Since in general \( n \ll N \), the procedure described above provides a powerful and efficient method for photoabsorption spectrum calculations without the need of determining and using the full \( N \times 1 \) eigenvectors.

5. Photoabsorption spectrum of chaotic diamagnetic hydrogen atoms

In this section, we present some numerical results for the oscillator strengths of the diamagnetic hydrogen atoms. Fig. 2 displays the oscillator strengths ranging from \(-40\) to \(-20\) cm\(^{-1}\). The field strength \( B \) is 5.9 T and the initial state is \( 2P_0 \). We use the shift
Fig. 2. The calculated oscillator strengths (in the energy range from $-40 \text{ cm}^{-1}$ to $-20 \text{ cm}^{-1}$) of diamagnetic Rydberg hydrogen atoms (initially at the $2P_0$ state) at $B=5.90 \text{ T}$.

Fig. 3. Same as fig. 2 except for the energy range from $-20 \text{ cm}^{-1}$ to $-10 \text{ cm}^{-1}$.

Fig. 4. Same as fig. 2 except for the energy range from $-10 \text{ cm}^{-1}$ to $0 \text{ cm}^{-1}$.

Fig. 4. Same as fig. 2 except for the energy range from $-10 \text{ cm}^{-1}$ to $0 \text{ cm}^{-1}$.

Results [13] is again achieved. The number of basis functions used is $N=6683$ (for fig. 3) and $N=9907$ (for fig. 4). This is the regime where the scaling energy $\epsilon = -\frac{E}{\gamma^{2/3}}$ is greater than the threshold $\epsilon_c = -0.127$ for the onset of classical chaos. The large increase in the number of basis functions needed for achieving convergence results from strong $n$ mixing and symmetry breaking in this classically chaotic regime. In our current calculation, all eigenvalues of interest are converged to within $10^{-8}$ au. Wunner et al. [14] and Wintgen [15] showed that the distribution of nearest-neighbor energy spacing changes from Poisson type to Wigner type when $\epsilon > \epsilon_c$. Our numerical results indicate that the procedure described in this work is capable of yielding not only eigenvalues but also oscillator strengths accurately and efficiently without the need of using the full eigenvectors of very large dimension ($N$).

We are now extending the work to the positive energy regime. Preliminary results for the oscillator strengths from the initial state $3S_0$ at $B=6.1143 \text{ T}$ below the first Landau threshold ($E=2.8 \text{ cm}^{-1}$) are again in good agreement with the experiment [3]. Above the first Landau threshold, all the bound states are imbedded in the continua and become autoionizing resonance states [16]. We are currently extending the complex scaling technique [16,17] along with the spectrum transform Lanczos algorithm to this resonance domain. As much as $150000$ basis
functions can be efficiently handled by this procedure. Detailed results and the underlying mechanisms for the mystery of the resurgence of symmetry in the classically chaotic regime will be explored in a subsequent work.

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References