Schrödinger equation of the hydrogen atom in strong magnetic fields

The problem

The time-independent Schrödinger equation of a hydrogen-like ion of nuclear charge Z and infinite nuclear mass is

$$\hat{H}\Psi = E\Psi,$$

where

$$\hat{H} = \frac{1}{2m_e}(\hat{p} - \frac{e}{c}\mathbf{A})^2 + eV$$

and

$$\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r}, \qquad \hat{p} = \mathrm{i}\hbar\nabla, \qquad V = -\frac{Z}{|\mathbf{r}|}.$$

Using cylindrical coordinates and atomic units $m_e = \hbar = e = 1$, $\omega = e|\mathbf{H}|/(2m_e c)$ in a homogeneous magnetic field ($\mathbf{H}$ is parallel to the axis z) the Hamiltonian takes the form

$$\hat{H}(\varrho, z) = -\frac{1}{2}\Delta + \frac{\omega n_3}{2} + \frac{\omega^2\varrho^2}{8} - \frac{Z}{\sqrt{\varrho^2 + z^2}}$$

when ($n_3 \in \mathbf{Z}$ is the magnetic quantum number),

$$\Psi(z, \varrho, \varphi) = (2\pi)^{-1/2}\exp(\mathrm{i}n_3\varphi)\psi(z, \varrho).$$

Thus, the eigenvalue problem is

$$\Big[\frac{\partial^2}{\partial\varrho^2} + \frac{1}{\varrho}\frac{\partial}{\partial\varrho} + \frac{\partial^2}{\partial z^2} - \frac{{n_3}^2}{\varrho^2} + \frac{2Z}{\sqrt{\varrho^2 + z^2}} - \omega^2\varrho^2 + 2E^*\Big]\psi = 0,$$

$$0 < \varrho < \infty, \quad -\infty < z < \infty, \quad E^* = E - \omega n_3.$$

Some historical aspects of the solutions

a) Variational methods

b) Diagonalization technique

c) Eigenfunction expansions

The problem in Liu-Starace basis

The representation

$$\psi(z,\varrho)=\sum_{n=0}^{\infty} f_n(z)\Phi_n(z,\varrho)$$

(Liu and Starace 1987).

$$\Big[\frac{\partial^2}{\partial\varrho^2}+\frac{1}{\varrho}\frac{\partial}{\partial\varrho}-\frac{{n_3}^2}{\varrho^2}+\frac{2Z}{\sqrt{\varrho^2+z^2}}-\omega^2\varrho^2+\mu(z)\Big]\Phi(z,\varrho)=0,$$
$$0<\varrho<\infty,\quad \Phi_n(z,\varrho)\ \text{ bounded } \forall z.$$

The LaS basis is orthonormalized by

$$\big(\Phi_{n'},\Phi_n\big)=\int_0^\infty \Phi_{n'}(\varrho)\Phi_n(\varrho)\varrho d\varrho=\delta_{n'n},\quad \forall z\in\mathbf{R}$$

In this case, $\{f_n(z)\}_{n=0}^{\infty}$ satisfies

$$\frac{d^2 f_n}{dz^2}+\Big[2E^*-\mu_n(z)\Big]f_n+\sum_{n'=0}^{\infty}\Big[A_{nn'}f_{n'}+B_{nn'}\frac{d\,f_{n'}}{dz}\Big]=0,$$
$$-\infty<z<\infty,\ n=0,1,\dots,$$

where

$$A_{nn'}(z) = \left(\Phi_n, \frac{\partial^2 \Phi_{n'}}{\partial z^2}\right), \quad B_{nn'}(z) = 2\left(\Phi_n, \frac{\partial \Phi_{n'}}{\partial z}\right)$$

and due to orthonormalization, $B_{nn} = 0$ and $B_{nn'} = -B_{n'n}$.

The advantages of LaS basis:

a) less N are sufficient for a fixed accuracy $\Longrightarrow$ easier to interpret physically

b) easy to get E_k^N for higher n_3, k,

c) easy to treat the problem analytically in the asymptotic ranges (see Barcza 1996).

Numerical treatment, results

Computation of $\mu_n(z)$, $A_{nn'}(z)$, $B_{nn'}(z)$ by a modified Prüfer transformation (Balla and Benkő 1996).

$\Longrightarrow$

a) without computing $\Phi_n(\varrho, z)$

b) without numerical derivations and integrations
for $A_{nn'}$, $B_{nn'}$

c) initial value problems for first order ODEs

d) in finite intervals.

For fixed N, $N = 1, 2, \ldots$, we investigate the eigenvalue problem

$$\frac{d^2 F^N}{dz^2} + \mathcal{B}(z)\frac{dF^N}{dz} + [\mathcal{A}(z) - \mathcal{M}(z)]F^N = -2E^{*N}F^N,$$
$$-\infty < z < \infty, \quad F^N \text{ bounded.}$$

The boundary conditions are either

$$F^N(0) = 0 \quad \text{(odd) or} \quad {F^N}'(0) = 0 \quad \text{(even)}$$

and

$$F^N(z) \;\text{ bounded if }\; z \to \infty.$$

$\Longrightarrow$

a) without computing $F^N(z)$
b) initial value problems for a system of first order ODEs
c) in finite intervals.

Problems

(1) Parametric Hilbert space defined by $\Phi_n(\varrho, z)$ is a complete space or not?

(2) How many eigenstates are below an arbitrary K bound for a fixed ω, n_3?

(3) $\sigma_{\mathrm{p}}(\hat{H}(\varrho, z)) \cap \sigma_{\mathrm{c}}(\hat{H}(\varrho, z)) = \emptyset$ for a fixed n_3?

The coupled equation

We reduce the problem to a finite interval: when $z \to \infty$ the boundedness of a solution $F^N(z)$ involves that

$$F^{N\prime}(z) = \alpha(z) F^N(z) \text{ for sufficiently large } z$$

where

$$\lim_{z\to\infty} \alpha^2(z) = \mathcal{M}_\infty - 2E^* I, \quad \alpha_\infty = \lim_{z\to\infty} \alpha(z)$$

should be chosen negative definite (see Birger and Lyalikova 1965). For the approximation of this, we may use the boundary condition

$$F^{N\prime}(z_\infty) = \alpha_\infty F^N(z_\infty)$$

Next, let us rewrite the odd and even problems in the form of

$$G' + \mathcal{P}(z, E^*) G = 0, \quad z_1 \le z \le z_\infty,$$

$$U_1^{\mathrm{l}i\mathrm{T}} G(z_1) = 0,$$

$$U_\infty^{\mathrm{rT}} G(z_\infty) = 0,$$

respectively, where

$$G = \begin{pmatrix} F^N \\ F^{N\prime} \end{pmatrix}, \ \ \mathcal{P}(z, E^*) = \begin{pmatrix} 0_N & -I_N \\ \mathcal{A} - \mathcal{M} + 2E^* I_N & \mathcal{B} \end{pmatrix},$$

$z_1 = z_0$ when $n_3 = 0$, otherwise $z_1 = 0$, i=e(=even), o=(odd).

$$U_1^{\mathrm{le}} = \begin{pmatrix} 0_N \\ I_N \end{pmatrix}, \ \ U_1^{\mathrm{lo}} = \begin{pmatrix} I_N \\ 0_N \end{pmatrix},$$

and the normalized right boundary condition,

$$U^{\mathrm{r}}_{\infty} = \begin{pmatrix} -(\alpha^{\mathrm{T}}_{\infty}\alpha_{\infty} + I_N)^{-1/2}\alpha_{\infty} \\ (\alpha^{\mathrm{T}}_{\infty}\alpha_{\infty} + I_N)^{-1/2} \end{pmatrix}.$$

The numerical problems were discussed in Abramov et al (1980). A vector function $G(z, E)$ is a solution if, for any $z \in [z_1, z_{\infty}]$, it satisfies the linear algebraic system

$$U^{\mathrm{l}i\mathrm{T}}(z)G(z,E) = 0, \quad U^{\mathrm{rT}}(z)G(z,E) = 0$$

where $(2N \times N)$ matrix functions $U^p(z)$, $p = \mathrm{l}i$, $i = \mathrm{o}$, e or $p = \mathrm{r}$ are the solutions of the initial value problems

$$U^{p\prime} - \left[I_{2N} - U^p(U^{p\mathrm{T}}U^p)^{-1}U^{p\mathrm{T}}\right]\mathcal{P}^{\mathrm{T}}U^p = 0$$

with initial values

$$U^{\mathrm{l}i}(z_1) = U^{\mathrm{l}i}_1, \quad U^{\mathrm{r}}(z_{\infty}) = U^{\mathrm{r}}_{\infty},$$

respectively. In turn, $G(z, E)$ is a non-trivial solution, i.e., E is an eigenvalue if

$$det \begin{pmatrix} U^{\mathrm{l}i\mathrm{T}}(z) \\ U^{\mathrm{rT}}(z) \end{pmatrix} = 0.$$

The basis equation

By transformation $\Phi(\varrho, z) = \sqrt{\varrho}\hat{\Phi}(\varrho, z)$

$$\Phi''(\varrho, z) + [q(\varrho, z) + \mu(z)]\Phi(\varrho, z) = 0,$$

where

$$q(\varrho, z) = \frac{\frac{1}{4} - {n_3}^2}{\varrho^2} + \frac{2Z}{(\varrho^2 + z^2)^{1/2}} - \omega^2\varrho^2.$$

First, we consider the case $z \neq 0$.

$$q(\varrho, z) = \frac{1}{\varrho^2}\sum_{i=0}^{\infty} q_i \varrho^{2i} \quad \text{if} \quad \frac{\varrho}{z} < 1,$$

$$q(\varrho, z) = \varrho^2 \sum_{i=0}^{\infty} \tilde{q}_i \varrho^{-i} \quad \text{if} \quad \frac{\varrho}{z} > 1,$$

The boundedness of any solution Φ $(\forall \varrho)$ at the ends of the interval $(0, \infty)$ is equivalent to the statements:

(i) for any sufficiently small ϱ $(\varrho \ll z)$,

$$\varrho\Phi'(\varrho) = \gamma(\varrho)\Phi(\varrho),$$

where

$$\gamma = \sum_{i=0}^{\infty} \gamma_i \varrho^{2i},$$

(Balla 1977).

(ii) for any sufficiently large ϱ $(\varrho \gg z)$,

$$\Phi'(\varrho) = \varrho\beta(\varrho)\Phi(\varrho),$$

where

$$\beta \sim \sum_{i=0}^{\infty} \frac{\beta_i}{\varrho^i},$$

due to Birger and Lyalikova (1965).

Thus, if a small $\varrho = \varrho_0$ and a large $\varrho = \varrho_\infty$ are fixed $\Longrightarrow$ equivalent eigenvalue problem formed of on $[\varrho_0, \varrho_\infty]$ This problem is free of singularities.

Now, we define functions $r(\varrho), \Theta(\varrho)$

$$\Phi(\varrho) = \frac{r(\varrho)}{\nu(\varrho)} \sin\Theta(\varrho), \quad \Phi'(\varrho) = \nu(\varrho) r(\varrho) \cos\Theta(\varrho).$$

This is a modified Prüfer transformation where $\nu(\varrho)$ is an almost arbitrary function. We arrive

$$\Theta' = \nu^2 \cos^2\Theta + \frac{1}{\nu^2}[q(\varrho, z) + \mu] \sin^2\Theta + \frac{(\nu^2)'}{\nu^2} \frac{\sin 2\Theta}{2}.$$

The initial conditions

$$\Theta(\varrho_0) = \arctan \frac{\varrho_0 \nu^2(\varrho_0)}{\gamma(\varrho_0)}$$

and

$$\Theta(\varrho_\infty) = -\arctan \frac{\varrho_\infty \beta(\varrho_\infty)}{\nu^2(\varrho_\infty)} + (n + \frac{1}{2})\pi.$$

Quadratic funtionals

Instead of computing the norm of the eigenfunctions, $A_{nn'}$ and $B_{nn'}$ by numerical integration, we split the integral into two parts (Kitoroage et al. 1987).

$$\int_0^{\varrho} \Phi^2(\xi, z)d\xi = {r_\mathrm{l}}^2(\varrho, z)h_\mathrm{l}(\varrho, z)$$

and

$$\int_{\varrho}^{\infty} \Phi^2(\xi, z)d\xi = -{r_\mathrm{r}}^2(\varrho, z)h_\mathrm{r}(\varrho, z).$$

Then

$$h_i'(\varrho) = \frac{1}{\nu^2(\varrho)} \sin^2\Theta_i(\varrho) + 2v_i(\varrho)h_i(\varrho), \qquad i = \mathrm{l}, \mathrm{r},$$

With the assumption of

$$h_\mathrm{l}(\varrho) = \sum_{j=1}^{\infty} h_\mathrm{l}^{(j)} \varrho^j$$

and

$$h_\mathrm{r}(\varrho) \sim \sum_{j=0}^{\infty} \frac{h_\mathrm{r}^{(j)}}{\varrho^j}$$

Having integrated the equations, we use the orthonormalization condition and get

$$r_\mathrm{c} = [h_\mathrm{l}(\varrho_\mathrm{c}) - h_\mathrm{r}(\varrho_\mathrm{c})]^{1/2}.$$

The normalization is taken into account without the computation of the eigenfunction to be normalized!

$A_{nn'}$, $B_{nn'}$ similarly.