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On a Class of Non-separable Quantum-Mechanical Eigenvalue Problems

Analytical and Technical Considerations within the Frame of a Born Expansion Method

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An idea of Born is reviewed and elaborated to non-separable quantum-mechanical eigenvalue problems in which the Schrödinger equation can be solved exactly for a subconfiguration. (By subconfiguration we mean a subsystem in which one dynamic variable of the whole system is considered as parameter; derivations with respect to this variable are omitted.) The eigenfunctions in the subconfiguration (e.g., the eigenfunctions of a Born–Oppenheimer approximation) are used as a basis to expand the eigenfunction of the complete problem. By analytical methods it is shown how to construct the complete ensemble of solutions which can be systematically mapped and classified by their analytical behaviour in one of the singularities (in a regular singularity). A modification of the Numerov procedure is given to the numerical solution of the coupled second-order ordinary differential equations which arise from our treatment. The analytical asymptotic solutions are used to bridge over the asymptotic regions in which the error of the Numerov procedure is large. As a concrete example the comprehensive asymptotic analysis of the Schrödinger equation of a hydrogen-like ion in strong homogeneous magnetic field is presented, practical methods and computational aspects are discussed, and finally a few actual numerical results are reported: some energy levels are given as a function of field strength.

1. INTRODUCTION

Many quantum-mechanical eigenvalue problems for E have the form

$$[D_1(\mathbf{y}, x) + D_2(x) - E]\, F(x, \mathbf{y}) = 0, \tag{1}$$

where $F(x, \mathbf{y})$ cannot be factorized in terms of the variables x and $\mathbf{y}$. D_1 and D_2 contain the potential(s) and differentiations with respect to $\mathbf{y}$ and x, respectively, x is a *parameter* of D_1, the general form

$$D_2(x) = k_2(x)\frac{\partial^2}{\partial x^2} + k_1(x)\frac{\partial}{\partial x} + k_0(x) \tag{2}$$

can be assumed. The eigenvalue E must be determined to the boundary conditions on F so that F must be regular in the whole range of the variables x, $\mathbf{y}$ and for bound states its norm must be

$$\langle F, F\rangle = \iint F^* F\, d\mathbf{y}\, dx = 1. \tag{3}$$

(The variable $\mathbf{y}$ can represent a set of variables. We assume $d\mathbf{y} = g(x)\, d\tilde{\mathbf{y}}$, where $g(x)$ is the x dependent part of $d\mathbf{y}$; it is fixed by our choice of coordinate system.)

2. INTRODUCTION TO A METHOD BY BORN TO SOLVE (1)

If the parametric eigenvalue problem

$$[D_1(\mathbf{y}, x) - \mu_\alpha(x)]\, \Phi_\alpha(x, \mathbf{y}) = 0, \qquad \alpha = 1, 2, \ldots, \tag{4}$$

is solved to the boundary conditions (imposed on Φ_α) which must be derived from the regularity requirement and (3) the solution of (1) can be postulated as

$$F(x, \mathbf{y}) = \sum_\alpha f_\alpha(x)\, \hat{\Phi}_\alpha(x, \mathbf{y}) \tag{5}$$

[1], where

$$\hat{\Phi}_\alpha(x, \mathbf{y}) = \hat{g}_\alpha(x)\, \Phi_\alpha(x, \mathbf{y}). \tag{6}$$

If (4) possesses continuous eigenvalues as well, an appropriate integral over these eigenfunctions must be supplemented to the sum in assumption (5).

The functions Φ_α build up an orthonormalized system at a fixed value of x for functions of $\mathbf{y}$. For the sake of generality and convenience they were normalized as

$$(\hat{\Phi}_\alpha, \hat{\Phi}_{\alpha'}) = \int \Phi_\alpha^* \Phi_{\alpha'}\, \tilde{g}_\alpha(x)\, d\tilde{\mathbf{y}} = \delta_{\alpha\alpha'},$$
$$\tilde{g}_\alpha(x) = g(x)\, \hat{g}_\alpha^2(x) \tag{7}$$

if $\alpha\alpha'$ refer to eigenfunctions with discrete eigenvalue.

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On introducing assumption (5) in (1) a projection onto $\hat{\Phi}_\alpha$—a multiplication by $\hat{\Phi}_\alpha^*$ and an integration over $\mathbf{y}$—results in the following coupled system of ordinary differential equations for $f_\alpha(x)$:

$$\int d\mathbf{y}\, \hat{\Phi}_\alpha^*(x, \mathbf{y})[D_2(x) + \mu_\alpha(x) - E] \sum_{\alpha'} f_{\alpha'}(x)\, \hat{\Phi}_{\alpha'}(x, \mathbf{y}) = 0$$

$$\alpha = 1, 2, \ldots. \qquad (8)$$

By a particular choice of $\hat{g}_\alpha(x)$ the form of the coupled differential equations for $f_\alpha(x)$ can be influenced, i.e., a part of $f_\alpha(x)$ can be a priori incorporated into the functions $\hat{\Phi}_\alpha$.

Using (5) and (7) in (3) we find for bound states that

$$\langle F, F\rangle = \sum_\alpha \int f_\alpha^2(x)/\hat{g}_\alpha^2(x)\, dx = \sum_\alpha f_{\langle\alpha\rangle}^2 = 1. \qquad (9)$$

We can regard our procedure—the expansion in terms of $\hat{\Phi}_\alpha$ and the solution of the equations arising from the projection—as convergent if the sum in (9) is convergent. This convergence can be inspected by numerical experience after having solved (8) numerically. The general proof of a convergence, if exists, is beyond the scope of the present paper.

The orthonormality of the functions $\hat{\Phi}_\alpha$ at fixed x does not mean automatically that they give a complete basis for expanding $F(x, \mathbf{y})$. It is, however, reasonable to expound the analytical and computational consequences of the choice of this basis and to compare the results with those coming from the use of other bases. A less complicated (more widely used) basis can be constructed in terms of a single variable—usually $\mathbf{y}$. If, e.g., hydrogen-like ions are treated in a strong magnetic field which is of the general form (1) when using the Legendre or Landau basis to expand the non-factorizable eigenfunction F of (1), in reality we use a sum of factorized functions in terms of the variables corresponding to x and $\mathbf{y}$ [2]. This inferior choice of the basis functions may be responsible for slow convergence and the large number of the necessary terms for obtaining moderate accuracy and for failure in some critical spectral regions, at the ionization thresholds, or at excited states.

As examples for problems of the general form (1)–(9) we can mention the Schrödinger equation:

(a) of a hydrogen-like ion in a homogeneous magnetic field (in spherical or cylindrical coordinates), in homogeneous electric or electric and magnetic fields which are parallel (in spherical coordinates),

(b) of a helium-like ion (in hyperspherical or in confocal elliptic coordinates), or

(c) of the ionized hydrogen molecule (in confocal elliptic coordinates) [3–6].

It is an interesting common feature of these problems that in one of the singular points of (8), e.g., at $x = 0$ if x represents a radius (this is a regular singularity) for the "expansion coefficient" $f_\alpha(x)$ *all asymptotic solutions* can be found exactly *by purely analytical and algebraic machinery.* On the condition whether these asymptotic solutions can be analytically extended to the whole range of the variable x we have an efficient tool for finding all eigenvalues and eigenstates (without any previous experimental knowledge of the spectrum of E). A further common feature of problems (a)–(c) that by inspecting the functions $f_\alpha(x)$ in the other singular point of (8) (at $x \to \infty$ if x represents a radius, this is an irregular singularity) approximate formulae can be obtained for the autoionizing levels.

Nomenclature, some remarks. A fixed value of the subscript α is frequently called channel, operator D_2 is the mixer among the channels. If in assumption (5) and consequently in (8) the sum $\sum_{\alpha'}$ is confined to the term $\alpha' = \alpha$ the approximation is called adiabatic. Since the non-diagonal matrix elements $(\hat{\Phi}_\alpha, D_2\hat{\Phi}_{\alpha'})$ are usually smaller than the diagonal ones the adiabatic approximation gives quite nice results frequently. The eigenvalue $\mu_\alpha(x)$ and the diagonal element $(\hat{\Phi}_\alpha, D_2\hat{\Phi}_\alpha)$ are additional "potentials" in a one-particle equation, their meaning can be well visualized. The main field of skill in applying the method is to construct D_1, D_2, and $\hat{g}_\alpha(x)$ in a manner that we have conveniently tractable equations when (4) and (8) are written down in the actual problem. It is of utmost importance that a singularity or singularities of the potential be incorporated into D_1, i.e., into (4); in doing so we encounter fewer problems when treating (8).

Since the principal idea of the method applied and elaborated in this section was first mentioned—to the author's knowledge—by Born [1] in the context of quantum mechanics of molecules and crystal lattices the specification as a Born expansion method is proposed to differentiate from the other Born methods known in other fields of quantum mechanics. The idea has been mentioned in the literature occasionally since its conception (e.g., [7]), its analytical consequences have not been exploited, and the coupled channel equations (8) have been solved for a limited number of problems: by a perturbative technique for H_2^+, $H\mu H$ in [8] while in [9] for similar molecules and even for two electron atoms a variational iterative solution was given. Coupled equations of type (8) have been discussed in [10] if the coupling did not contain $df_{\alpha'}/dx$. By the subsequent sections we want to demonstrate that by much analysis, algebra, and moderate computing efforts it is possible to treat involved problems if (8) is solved by a direct numerical integration. The Schrödinger equation of a hydrogen atom of infinite nuclear mass in strong external magnetic field is a simple quantum mechanical example of the form of (1) if it is written in spherical coordinates.

We shall use this example to give an impression of how our general analytical considerations and our numerical procedure work in practice.

The relation of our method to the more familiar and widely used Born–Oppenheimer approximation is discussed in [11]. The essence of the difference is that in a Born–Oppenheimer approximation

$$\frac{d}{dx}\left[\mu_\alpha(x)+k_0(x)\right]|_{x=x^*}=0, \qquad 0<x^*<\infty, \quad (10)$$

is a necessary condition which is not met in our problems (a) and (b). (The ionized hydrogen molecule can be treated in Born–Oppenheimer approximation or in the Born expansion method as well. The first approach is expected to be convenient and accurate for low-lying vibrational levels while the second approach promises perhaps satisfactory results near the dissociation limit.)

3. THE ASYMPTOTIC BEHAVIOUR OF EQ. (4) AND $f_\alpha(x)$ IN THE SINGULAR POINTS $x^{(1)}$ AND $x^{(2)}$ OF EQ. (1)

By postulation (5) the regular behaviour of F is provided in the singular points of the space of $\mathbf{y}$ automatically because the basis functions $\Phi_\alpha(x, \mathbf{y})$ are regular in any point $\mathbf{y}$ independently from the value of x. Therefore, we have to deal with the singularities on the axis x. Usually a canonical (quantum mechanical) eigenvalue problem is described by (4) in the singular points $x^{(1)}$ or $x^{(2)}$ of (1) or in both points. This feature offers a possibility to expand the eigenvalues $\mu_\alpha(x)$ and eigenfunctions $\Phi_\alpha(x, \mathbf{y})$ in terms of (a power of) Δx:

$$\mu_\alpha(\Delta x^{(j)})=\sum_{m=m_0}^{\infty} a_{\alpha,j}^{(m)}\,\Delta x^{(j)m} \quad (11)$$

$$\Phi_\alpha(x, \mathbf{y})=\sum_{\alpha'} b_{\alpha',j}(\Delta x^{(j)})\,\Phi_{\alpha'}(x^{(j)}, \mathbf{y}), \qquad j=1, 2, \quad (12)$$

$$\Delta x^{(j)}=x^{s_j},$$

where s_j is an integer number (positive if $x^{(1)}=0$, negative if $x^{(2)}=\infty$) and

$$b_{\alpha',j}(\Delta x^{(j)})=\delta_{\alpha\alpha'}+\sum_{m=1}^{\infty} b_{\alpha',j}^{(m)}\,\Delta x^{(j)m} \quad (13)$$

if $\Delta x^{(j)} \ll 1$. On introducing (11)–(13) in (4), using the interrelations among the functions $\Phi_\alpha(x^{(j)}, \mathbf{y})$ and their derivatives with different subscripts α, multiplying (4) by $\Phi_\alpha^*(x^{(j)}, \mathbf{y})$, and integrating it over $\mathbf{y}$, we obtain a system of linear algebraic equations for the unknown coefficients $a_{\alpha,j}^{(m)}$, $b_{\alpha',j}^{(m)}$ which can be solved by some labour.

As the next step expansion (12) can be directly used to calculate asymptotic power series expansions in terms of $\Delta x^{(j)}$ for the coupling matrix elements coming from $(\hat{\Phi}_\alpha, D_2\hat{\Phi}_{\alpha'})$. If these asymptotic expressions and (11) are introduced in (8) and the constraints on $f_\alpha(x^{(j)})$, $\alpha=1, 2, \ldots$, from the regularity requirement of F are taken into account we are at least able to indicate the shape of $f_\alpha(\Delta x^{(j)})$ at $0 \leqslant \Delta x^{(j)} \ll 1$ and in the regular singularity of (8) *we are able to construct the complete ensemble of the possible forms of* $f_\alpha(x)$, $\alpha=1, 2, \ldots$, e.g., as power series in terms of $\Delta x^{(j)}$. By this procedure *all asymptotic solutions F have been found in one of the singularities.* As the last step it must be surveyed (numerically) whether these asymptotic solutions can be analytically extended to the whole range $x^{(1)} \leqslant x \leqslant x^{(2)}$ so that F is regular and (3) is satisfied for bound states.

If the expansions (11)–(13) exist all solutions turned out to (1) by our briefly described analytical and algebraic machienery and they can be classified very naturally, e.g., by the number of the nodes of $\Phi_n(x, \mathbf{y})$ (which is invariant in the interval $x^{(1)} \leqslant x \leqslant x^{(2)}$) and by the weight of this component expressed through the shape (or value) of $f_\alpha(x)$ at $0 \leqslant \Delta x^{(j)} \ll 1$ ($j=1$ or $j=2$). Consequently the solutions to (1) can be systematically mapped and solutions cannot be overlooked since there exist no other regular solutions in one of the singularities. In contrast to this advantage we mention that in a variational or other traditional solution of (1) (e.g., by diagonalization) the initial assumptions, choice of trial (basis) functions (nowadays frequently consisting of some thousand elements) involve some prerequisite limitations and non-transparency, therefore, solutions (whether all (?) or rather a few ones only) can be found which are within the preset limitations, a systematical mapping of solutions is not available and the physical meaning of a successful trial function (e.g., containing even quadratically integrable singularities) is not clear. By the choice of our basis functions $\hat{\Phi}_\alpha$ the system of Eqs. (8) seems to possess non-transparency only which is inherent to our original problem (1).

4. SOME TECHNICAL DETAILS OF SOLVING (8)

After having discussed the analytical features of the solutions of (8) in the singular points on the axis x we turn to determining the solutions on the whole axis x. Equation (8) is a system of coupled second-order ordinary differential equations of the form

$$f_\alpha''+\left[\frac{k_1}{k_2}+B_{\alpha\alpha}\right]f_\alpha'+\left[A_{\alpha\alpha}+\frac{k_0+\mu_\alpha-E}{k_2}\right]f_\alpha$$

$$+\sum_{\alpha'}{}' \left[A_{\alpha\alpha'}f_{\alpha'}+B_{\alpha\alpha'}f_{\alpha'}'\right]=0 \qquad \alpha=1, 2, \ldots, \quad (14)$$

where

$$B_{\alpha\alpha'}(x) = 2\left(\hat{\Phi}_\alpha, \frac{\partial \hat{\Phi}_{\alpha'}}{\partial x}\right)$$

$$A_{\alpha\alpha'}(x) = \left(\hat{\Phi}_\alpha, \frac{\partial^2 \hat{\Phi}_{\alpha'}}{\partial x^2}\right) + \frac{k_1}{k_2}\left(\hat{\Phi}_\alpha, \frac{\partial \hat{\Phi}_{\alpha'}}{\partial x}\right)$$

and $\sum'$ indicates that the term $\alpha = \alpha'$ must be omitted in the summation.

4.1. If $\alpha \neq \alpha'$ the calculation of the coupling matrix elements in $A_{\alpha\alpha'}$ and $B_{\alpha\alpha'}$ can be simplified because D_1 is a hermitian operator. A derivation of (4) with respect to x, a multiplication by $\Phi^*_{\alpha'}(x, \mathbf{y})$, and an integration over $\mathbf{y}$ results in the relation

$$\left(\Phi_{\alpha'}, \frac{\partial \Phi_\alpha}{\partial x}\right) = \left(\Phi_{\alpha'}, \frac{\partial D_1}{\partial x}\Phi_\alpha\right) \Big/ [\mu_\alpha(x) - \mu_{\alpha'}(x)], \quad (15)$$

where $\partial D_1/\partial x$ indicates that the parametric part of D_1 (in x) must be derived and all other parts of D_1 must be omitted. The same steps once more give

$$\left(\Phi_{\alpha'}, \frac{\partial^2 \Phi_\alpha}{\partial x^2}\right) = \left\{2\left(\Phi_{\alpha'}, \left[\frac{\partial D_1}{\partial x} - \frac{d\mu_\alpha}{dx}\right]\frac{\partial \Phi_\alpha}{\partial x}\right) + \left(\Phi_{\alpha'}, \frac{\partial^2 D_1}{\partial x^2}\Phi_\alpha\right)\right\} \Big/ [\mu_\alpha(x) - \mu_{\alpha'}(x)]. \quad (16)$$

4.2. If $\alpha = \alpha'$ we obtain from (7)

$$\left(\hat{\Phi}_\alpha, \frac{\partial \hat{\Phi}_\alpha}{\partial x}\right) = \int \Phi^*_\alpha \frac{\partial \Phi_\alpha}{\partial x}\tilde{g}_\alpha \, d\tilde{\mathbf{y}} = -\frac{1}{2\tilde{g}_\alpha(x)}\frac{d\tilde{g}_\alpha}{dx} \quad (17)$$

and

$$\int \Phi^*_\alpha \frac{\partial^2 \Phi_\alpha}{\partial x^2}\tilde{g}_\alpha \, d\tilde{\mathbf{y}} + \int \left(\frac{\partial \Phi_\alpha}{\partial x}\right)^2 \tilde{g}_\alpha \, d\tilde{\mathbf{y}} = \left(\frac{1}{\tilde{g}_\alpha(x)}\frac{d\tilde{g}_\alpha}{dx}\right)^2 - \frac{1}{2\tilde{g}_\alpha(x)}\frac{d^2\tilde{g}_\alpha}{dx^2}. \quad (18)$$

By (15)–(18) we have to compute fewer derivatives of Φ_α for $A_{\alpha\alpha'}$ and $B_{\alpha\alpha'}$.

4.3. We can solve (14) by direct numerical integration as follows. If $B_{\alpha\alpha'}(x) \equiv 0$ for all $(\alpha\alpha')$ the direct numerical integration of equations of type (14) is possible by the efficient Numerov procedure [10]. If, however, $B_{\alpha\alpha'} \not\equiv 0$ lower order procedures were proposed only, e.g., a Runge–Kutta–Nyström procedure [12]. Now we shall reconcile the Numerov procedure with the presence of $f'_{\alpha'}$ in (14).

The Numerov procedure [13] was constructed to integrate numerically equations of the form

$$v''(x) = w(x)\, v(x) + z(x) \quad (19)$$

by the use of the three point recurrence relation

$$\left[1 - \frac{h^2}{12}w_{m+1}\right]v_{m+1} - \left[2 + \frac{5}{6}h^2 w_m\right]v_m + \left[1 - \frac{h^2}{12}w_{m-1}\right]v_{m-1} - \frac{h^2}{12}[z_{m+1} + 10z_m + z_{m-1}] + O\left(\frac{h^6}{240}v^{\mathrm{VI}}\right) = 0. \quad (20)$$

A derivation of (20), error estimations for one step, and recipes to vary the step size h were given in [14]. By the transformation

$$v^{(\alpha)}(x) = \exp\left\{\int_{x_0}^{x} d\tilde{x}\left[\frac{k_1(\tilde{x})}{2k_2(\tilde{x})} + \frac{B_{\alpha\alpha}(\tilde{x})}{2}\right]\right\} f_\alpha(x), \quad (21)$$

Eqs. (14) take the form (19)–(20) at each value of α if

$$w_m^{(\alpha)} = \frac{E - k_0 - \mu_\alpha}{k_2} - A_{\alpha\alpha} + \left[\frac{k_1}{2k_2} + \frac{B_{\alpha\alpha}}{2}\right]^2 + \frac{1}{2k_2}\left[\frac{dk_1}{dx} - \frac{k_1}{k_2}\frac{dk_2}{dx}\right] + \frac{1}{2}\frac{dB_{\alpha\alpha}}{dx} \quad (22)$$

$$z_m^{(\alpha)} = \sum_{\alpha'}{}' \left[\left(\frac{k_1}{2k_2} + \frac{B_{\alpha\alpha}}{2}\right)B_{\alpha\alpha'} - A_{\alpha\alpha'}\right]v^{(\alpha')} - B_{\alpha\alpha'}v^{(\alpha')'}, \quad (23)$$

where all symbols depending on x in the right side of (22), (23) must be taken in the point $x = x_m$. Finally $v^{(\alpha')'}(x_{m+1})$ must be eliminated from (23) in order to have complete harmony with (19) and (20). This was done by a three-point (predictor) formula

$$v_{m+1}^{(\alpha)'} = (9v_{m+1}^{(\alpha)} - 16v_m^{(\alpha)} + 7v_{m-1}^{(\alpha)})/(2h) - (8v_m^{(\alpha)''} + v_{m-1}^{(\alpha)''})\, h/3 + O(h^5 v^{\mathrm{v}}), \quad (24)$$

which was constructed according to the recipes in [15], $v_m^{(\alpha)''}$, $v_{m-1}^{(\alpha)''}$ were obtained from $v_m^{(\alpha)}$, $v_{m-1}^{(\alpha)}$ by (19). If (22)–(24) are introduced in (20) we obtain a system of linear algebraic equations for $v_{m+1}^{(\alpha)}$ which was solved by standard procedures for each step $m = 1, 2, \ldots$.

A final point is that we have to heed the non-trivial problem of starting the Numerov procedure because a three-point recursive formula like (20) is not self-starting in contrast, e.g., to a Runge–Kutta procedure. By our asymptotic considerations of the previous section we have, however, the complete set of $A_{\alpha\alpha'}(x^{(j)})$, $B_{\alpha\alpha'}(x^{(j)})$, $f_\alpha(x^{(j)})$,

either for $j=1$ or for $j=2$. Consequently our asymptotic expansions delivered just the necessary munition to calculate the terms occurring in (20)–(24) at x_0 and $x_1=x_0+h$. Starting (20) from $m=1$ (14) was solved by a shooting method: E is a free parameter, it was varied and $F(x_s, \mathbf{y})$; i.e., the set of $f_\alpha(x_s)$ was surveyed whether the boundary condition is satisfied at $x_s \to x^{(2)}$ if we started the integration from $x_0=x^{(1)}$. If the error term in (20) was large in the neighbourhood of $x^{(1)}$ or $x^{(2)}$ we used our asymptotic expansions for some further points $1<m<m'$.

In actual calculations the permitted relative error of $v_{m+1}^{(\alpha)}$ in a step was fixed. The step size was varied according to this error to economize with the computing time; for details see [14], where $z(x)=0$ was assumed. With our $z\neq 0$ the error estimations of [14] remain, however, true. In comparison to (24) more sophisticated formulae were used as well, containing more backward points, or corrector type terms with $v_{m+1}^{(\alpha)''}$. By experience, however, it was found that (24) is in full harmony with the error of (20), i.e., (20) and (24) are fully compatible because the error of (24) is multiplied by $h^2/12$ in (20). A few actual numerical results will be presented in the following section.

5. AN EXAMPLE

Now we want to demonstrate how to use our general analytic considerations and modified Numerov procedure in a concrete problem. In this section all data are given in atomic units.

The Schrödinger equation of a hydrogen atom with infinite nuclear mass of charge $Z(=1)$ in a homogeneous magnetic field $\mathbf{H}$ parallel to the axis z is

$$-\frac{\partial}{\partial r} r^2 \frac{\partial \psi}{\partial r} + (\omega^2 r^4 - 2E^* r^2 - 2Zr)\,\psi - \frac{\partial}{\partial \eta}(1-\eta^2)\frac{\partial \psi}{\partial \eta} + \left(\frac{n_3^2}{1-\eta^2} - \omega^2 r^4 \eta^2\right)\psi = 0, \tag{25}$$

$$E^* = E - \omega n_3,$$

$$\eta = \cos\theta,$$

where r and θ are the spherical coordinates, the nucleus is in the origin, n_3 is the magnetic quantum number, $\omega = e\,|\mathbf{H}|/(2mc)$ is the Larmor frequency, $\omega=1$ if $|\mathbf{H}| = 4.70\times 10^5 T$, and (25) can be derived by elementary operations from [16].

We assume the even and odd solutions to (25) in the form

$$\psi(r,\eta) = \sum_{l'=|n_3|}^{\infty} f_{2l'+p}(r)\,\Phi_{2l'+p}(\eta, r) \tag{26}$$

by which (14) takes the form

$$f_l'' + \frac{2}{r} f_l' + \left[2E^* + \frac{2Z}{r} - \frac{\nu^2-\mu_l}{r^2} + A_{ll}\right] f_l + \sum_{l'}{}' \left[A_{ll'} f_{l'} + B_{ll'} f_{l'}'\right] = 0,$$

$$l = |n_3| + p,\ |n_3| + p + 2, \ldots \tag{27}$$

with

$$B_{ll'}(r) = 4\omega r\left(\Phi_l, \frac{\partial \Phi_{l'}}{\partial \nu}\right)$$

and

$$A_{ll'}(r) = 4\omega^2 r^2\left(\Phi_l, \frac{\partial^2 \Phi_{l'}}{\partial \nu^2}\right) + 6\omega\left(\Phi_l, \frac{\partial \Phi_{l'}}{\partial \nu}\right),$$

where $\Phi_l(\eta, \nu)$ is defined by the differential equation for the angular oblate spheroidal function

$$\left[\frac{\partial}{\partial \eta}(1-\eta^2)\frac{\partial}{\partial \eta} - \frac{n_3^2}{1-\eta^2} + \nu^2\eta^2 - \mu(\nu)\right]\Phi(\eta,\nu) = 0, \qquad \nu^2 = \omega^2 r^4 \tag{28}$$

[17], which is the second part of (25) and p is a parity quantum number of the solution (zero for even, one for odd functions Φ). Equation (28) has discrete eigenvalues only; its eigenfunctions will be normalized as

$$(\Phi_l, \Phi_{l'}) = \int_{-1}^{1} \Phi_l \Phi_{l'}\, d\eta = \delta_{ll'} \tag{29}$$

for any $0 \leqslant \nu \leqslant \infty$ in order to have

$$B_{ll}(r) = 0. \tag{30}$$

5.1. Asymptotic Analysis

Equations (25) and (27) have a regular singularity at $r=0$ and an irregular one at $r=\infty$.

5.1.1. In the domain $0 \leqslant \nu \ll 1$ we assume the eigenfunctions of (28) as

$$\Phi(\eta,\nu) = \sum_{m=|n_3|}^{\infty} \left[(-1)^{(l-|n_3|-p)/2}\,\delta_{ml} + D_m \nu^2 + \cdots\right] \times P_m^{|n_3|}(\eta), \tag{31}$$

with the eigenvalue

$$\mu = -l(l+1) + D_\mu^{(0)} \nu^2 + \cdots. \tag{32}$$

On introducing assumptions (31) and (32) in (28) we find that

$$\sum_{m=|n_3|}^{\infty}\Big\{[-m(m+1)+l(l+1)-D_\mu^{(0)}v^2+O(v^4)]\times[\delta_{ml}+D_m v^2+O(v^4)]\,P_m^{|n_3|}+v^2\Big[\frac{m+|n_3|}{2m+1}\frac{m+|n_3|-1}{2m-1}P_{m-2}^{|n_3|}+\Big(\frac{m^2-n_3^2}{4m^2-1}+\frac{(m+1)^2-n_3^2}{(2m+1)(2m+3)}\Big)P_m^{|n_3|}+\frac{m-|n_3|+1}{2m+1}\frac{m-|n_3|+2}{2m+3}P_{m+2}^{|n_3|}\Big]\times[\delta_{ml}+D_m v^2+O(v^4)]\Big\}=0. \tag{33}$$

In (33) we pick up the different powers of v first and next equate the coefficients of the different Legendre polynomials with zero. This procedure gives the results

$$\mu_l=-l(l+1)+\Big(\frac{l^2-n_3^2}{2l-1}+\frac{(l+1)^2-n_3^2}{2l+3}\Big)\times\frac{v^2}{2l+1}+O(v^4) \tag{34}$$

and

$$\Phi_l=N_l\sum_{m=0}^{\infty}v^{2m}\sum_{m'=-m}^{m}D_{l+2m'}^{(m)}P_{l+2m'}^{|n_3|} \tag{35}$$

where

$$N_l=\Big[\frac{(2l+1)(l-|n_3|)!}{2(l+|n_3|)!}\Big]^{1/2}$$

and a few coefficients can be given explicitly:

$$D_{l+2m}^{(m)}=(-1)^{(l-|n_3|-p)/2}\frac{(l+2m-|n_3|)!}{(l-|n_3|)!}\times\prod_{k=1}^{m}[2k(2l+2k+1)(2l+4k-1)\times(2l+4k-3)]^{-1},$$

$$D_{l-2m}^{(m)}=(-1)^{m+(l-|n_3|-p)/2}\frac{(l+|n_3|)!}{(l-2m+|n_3|)!}\times\prod_{k=1}^{m}[2k(2l-2k+1)(2l-4k+3)\times(2l-4k+5)]^{-1},\qquad m=0,1,2,\ldots.$$

The normalization (29) requires $D_l^{(1)}=0$ in (35).

Eigenfunctions (35) can be used directly to calculate the coupling matrix elements. If $l\neq l'$

$$\Big(\Phi_l,\frac{\partial^k\Phi_{l'}}{\partial v^k}\Big)=N_lN_{l'}v^{|l-l'|-k}\times\sum_{m=0}^{(1/2)|l-l'|-1}\frac{2(l\pm2m+|n_3|)!}{(l\pm2m-|n_3|)!\,(2l\pm4m+1)}\times\frac{(|l'-l|-2m)!}{(|l'-l|-2m-k)!}\times D_{l\pm2m}^{(m)}D_{l'\mp(|l'-l|-2m)}^{(|l'-l|/2-m)}+\cdots,\qquad k=1,2. \tag{36}$$

(In (36) the upper sign refers to $l'>l$.) If $l=l'$ we find from (18) directly that

$$\Big(\Phi_l,\frac{\partial^2\Phi_l}{\partial v^2}\Big)=-\Big[\frac{(l+2+|n_3|)!\,(l+2-|n_3|)!}{(2l+3)^4\,(2l+5)(l-|n_3|)!\,(l+|n_3|)!}+\frac{(l+|n_3|)!\,(l-|n_3|)!}{(2l-1)^4\,(2l-3)(l-2-|n_3|)!\,(l-2+|n_3|)!}\Big]\times\frac{v^2}{2l+1}+O(v^4). \tag{37}$$

5.1.2. At $r\ll1$ we assume

$$f_l(r)=r^{\gamma_l}\sum_{m=0}^{\infty}c_m^{(l)}r^m. \tag{38}$$

On introducing (34) and (38) in (27) we find that

$$\sum_{m=0}^{\infty}(\gamma_l+m)(\gamma_l+m+1)\,c_m^{(l)}r^{\gamma_l+m-2}+\Big[2E^*+\frac{2Z}{r}-\frac{l(l+1)}{r^2}+\frac{\omega^2}{2l+1}\times\Big(\frac{l^2-n_3^2}{2l-1}+\frac{(l+1)^2-n_3^2}{2l+3}\Big)r^2-\omega^2r^2+O(r^6)\Big]\times\sum_{m=0}^{\infty}c_m^{(l)}r^{\gamma_l+m}+\sum_{l'}{}'\Big[A_{ll'}\sum_{m=0}^{\infty}c_m^{(l')}r^{\gamma_{l'}+m}+B_{ll'}\sum_{m=0}^{\infty}(\gamma_{l'}+m)\times c_m^{(l')}r^{\gamma_{l'}+m-1}\Big]=0. \tag{39}$$

By (36), (37) we obtain series expansion for $A_{ll'}$, $B_{ll'}$ as

$$B_{ll'}=\sum_{m=0}^{\infty}B_{ll'}^{(4m+2|l-l'|-1)}r^{4m+2|l-l'|-1} \tag{40}$$

$$A_{ll'}=\sum_{m=0}^{\infty}A_{ll'}^{(4m+2|l-l'|-2)}r^{4m+2|l-l'|-2} \tag{41}$$

if $l \neq l'$ and

$$A_{ll} = \sum_{m=0}^{\infty} A_{ll}^{(4m+6)} r^{4m+6}. \tag{42}$$

At $r=0$ regular eigenfunctions ψ are obtained if in Eqs. (39) the coefficient of the lowest power of r vanishes which is provided by

$$\gamma_l = l \tag{43}$$

at an arbitrary value of $c_0^{(l)}$. This is in accordance with the vanishing of the diamagnetic "perturbation" $\omega^2 r^4 \eta^2$ in (25) at $r=0$. We have two types of asymptotic solutions.

Solution A. If more than one coefficient $c_0^{(l)}$ differs from zero the corresponding functions $f_l(r)$ are hydrogenic eigenfunctions even up to some further powers of r; i.e., the coupling of Eqs. (27) takes place only in higher powers of r because of the form (40)–(42) of the coupling matrix elements. In other words, Eqs. (39) are completely decoupled at $r=0$, the coefficients $c_0^{(l)}$ are undetermined, and this solution is equivalent to an arbitrary superposition of hydrogen-like $f_l(r)$ coefficients in the interval $0 \leqslant r \ll 1$. After having fixed the non-zero coefficients $c_0^{(l)}$ the asymptotic solution is a unique function with E as a parameter. By (40)–(43) in (39) we find for the first few coefficients $c_m^{(l)}$ of the channel with the lowest value of l,

$$\begin{aligned}(m+2)(2l+m+3)\, c_{m+2}^{(l)} + 2Zc_{m+1}^{(l)} + 2E^* c_m^{(l)} \\ + \left[\frac{\omega^2}{2l+1}\left(\frac{l^2-n_3^2}{2l-1} + \frac{(l+1)^2-n_3^2}{2l+3}\right) - \omega^2\right] c_{m-2}^{(l)} \\ = 0, \qquad m = -2, ..., 3,\end{aligned} \tag{44}$$

while

$$\begin{aligned}(m+2)(2l+m+3)\, c_{m+2}^{(l)} + 2Zc_{m+1}^{(l)} + 2E^* c_m^{(l)} \\ + [A_{l,l-2}^{(2)} + (l-2+m)\, B_{l,l-2}^{(3)}]\, c_m^{(l-2)} \\ = 0, \qquad m = -2, -1, 0, 1,\end{aligned} \tag{45}$$

is valid for the other channels and $c_m^{(l)} = 0$ for any l if $m < 0$.

Solution B. The singular point $r=0$ of (25) coincides with the force free problem ($\mathbf{H}=0$) in which l is a good quantum number and the hydrogen-like ion is in a state with definite quantum numbers. Therefore, it seems reasonable to treat the special case

$$c_0^{(l')} = \delta_{ll'}, \qquad l' = |n_3| + p, |n_3| + p + 2, ... \tag{46}$$

separately. By the value of l we defined the dominant term of the expansion (26). As compared to Solution A the non-dominant terms $f_{l \pm 2k}(r)$, $k = 1, 2, ...$, vanish much more rapidly at $r=0$. For the coefficients $c_m^{(l)}$ of the dominant term (44) is valid with $m = -2, -1, ..., 5$, while the expansion of the subordinate terms is

$$f_{l+2k}(r) = \sum_{m=0}^{\infty} c_{2k+m}^{(l+2k)} r^{l+4k+m}, \tag{47}$$

where the first few coefficients are

$$\begin{aligned}c_{2k+k'}^{(l+2k)} = \frac{-1}{2k(2l+6k+1) + k'(2l+8k+k'+1)} \\ \times \Bigg\{ 2E^* c_{2k+k'-2}^{(l+2k)} + 2Zc_{2k+k'-1}^{(l+2k)} \\ + \sum_{m=0}^{k-1} [A_{l+2k,l+2m}^{(4k-4m-2)} + (l+2m+k') \\ \times B_{l+2k,l+2m}^{(4k-4m-1)}]\, c_{2m+k'}^{(l+2m)} \Bigg\}, \\ k = 1, 2, ..., \qquad k' = 0, 1, 2, 3,\end{aligned}$$

and

$$f_{l-2k}(r) = \sum_{m=0}^{\infty} c_{6k+m}^{(l-2k)} r^{l+4k+m}, \tag{48}$$

where

$$\begin{aligned}c_{6k+k'}^{(l-2k)} = \frac{-1}{6k(2l+2k+1) + k'(2l+8k+k'+1)} \\ \times \Bigg\{ 2E^* c_{6k+k'-2}^{(l-2k)} + 2Zc_{6k+k'-1}^{(l-2k)} \\ + \sum_{m=0}^{k-1} [A_{l-2k,l-2m}^{(4k-4m-2)} + (l+4m+k') \\ \times B_{l-2k,l-2m}^{(4k-4m-1)}]\, c_{6m+k'}^{(l-2m)} \Bigg\}, \\ k = 1, 2, ..., l/2, \qquad k' = 0, 1, 2, 3.\end{aligned}$$

5.1.3. In the domain $v \to \infty$ we use

$$u = 2v(\eta + 1). \tag{49}$$

The transformation

$$\Phi = (1-\eta^2)^{|n_3|/2} \exp\{-u/2\}\, L(u) \tag{50}$$

puts (28) in the form

$$2vu\frac{d^2L}{du^2}+2(|n_3|+1-u)\,v\frac{dL}{du}$$
$$+\frac{1}{2}[v^2-\mu-(|n_3|+2v)|(|n_3|+1)]\,L$$
$$-u\left\{u\frac{d^2L}{du^2}+[2(|n_3|+1)-u]\frac{dL}{du}\right.$$
$$\left.-(|n_3|+1)\,L\right\}=0. \tag{51}$$

If $v\to\infty$ and

$$v^2-\mu-(|n_3|+2v)(|n_3|+1)$$
$$=4vq,\qquad q=0,1,2,..., \tag{52}$$

(51) admits the solution

$$L(u)\to L_{q+|n_3|}^{|n_3|}(u) \tag{53}$$

which leads to a regular Φ, where $L_{q+|n_3|}^{|n_3|}$ is an associated Laguerre polynomial. Therefore, for $v\to\infty$ we assume the eigenvalue in the form

$$\mu=v^2+\sum_{k=-1}^{\infty}c_{-k}v^{-k} \tag{54}$$

while the eigenfunction is

$$L(u)=\sum_{m=0}^{\infty}v^{-m}\sum_{m'=-m}^{m}\hat{D}_{q+m'}^{(m)}L_{q+m'+|n_3|}^{|n_3|}(u). \tag{55}$$

On putting assumptions (54) and (55) in (51), using some interrelations among associated Laguerre polynomials, picking up the different powers of v^{-1}, and equating the coefficients of the different Laguerre polynomials with zero, we find that

$$\mu=v^2-2(2q+|n_3|+1)\,v+2q(q+|n_3|+1)+|n_3|+1$$
$$+[(q+1)^2\,(q+1+|n_3|)^2-q^2(q+|n_3|)^2]/(4v)$$
$$+[(q+1)^2\,(q+1+|n_3|)^2\,(2q+|n_3|+2)$$
$$-q^2(q+|n_3|)^2\,(2q+|n_3|)]/(8v^2)+O(v^{-3}) \tag{56}$$

and

$$\Phi_q(\eta,v)=\left[\frac{2v^{|n_3|+1}q!}{(q+|n_3|)!^3}\right]^{1/2}(1-\eta^2)^{|n_3|/2}$$
$$\times\exp\{-v(\eta+1)\}\,L(u) \tag{57}$$

and a few coefficients can be given explicitly:

$$\hat{D}_{q+m}^{(m)}=(-1)^{m+q+p+1}\frac{(q+m)!}{4^m m!\,q!}$$

$$\hat{D}_{q-m}^{(m)}=(-1)^{q+p+1}\frac{q!\,(q+|n_3|)!^2}{4^m m!\,(q-m)!\,(q-m+|n_3|)!^2}.$$

The leading term of the expansion of the coupling matrix elements is

$$\left(\Phi_q,\frac{\partial\Phi_{q'}}{\partial v}\right)=\frac{(q!\,q'!)^{1/2}}{[(q+|n_3|)!\,(q'+|n_3|)!]^{3/2}}\,v^{-k}$$
$$\times\sum_{m=0}^{k-1}\frac{(q\pm m+|n_3|)!^3}{2(q\pm m)!}$$
$$\times\hat{D}_{q\pm m}^{(m)}\hat{D}_{q'\mp(k-m-1)}^{(k-m-1)}$$
$$\times\begin{cases}-(q+m+|n_3|+1)^2\\(q-m)/(q-m+|n_3|)\end{cases}+\cdots \tag{58}$$

and

$$\left(\Phi_q,\frac{\partial^2\Phi_{q'}}{\partial v^2}\right)=\frac{1}{2v^2}[-[(|n_3|+1)/2+q(q+|n_3|+1)]\,\delta_{qq'}$$
$$-[(q+1)(q+|n_3|+1)]^{1/2}\,\delta_{q,q'-1}$$
$$+[q(q+|n_3|)]^{1/2}\,\delta_{q,q'+1}]$$
$$+\frac{(q!\,q'!)^{1/2}}{4v^k[(q+|n_3|)!\,(q'+|n_3|)!]^{3/2}}$$
$$\times\sum_{m=0}^{k-2}\frac{(q\pm m+|n_3|)!^3}{(q\pm m)!}$$
$$\times\hat{D}_{q\pm m}^{(m)}\hat{D}_{q'\mp(k-m-2)}^{(k-m-2)}$$
$$\times\begin{cases}\begin{pmatrix}(q+m+|n_3|+2)^2\\\times(q+m+|n_3|+1)^2\end{pmatrix}\\\dfrac{(q-m)(q-m-1)}{(q-m+|n_3|-1)(q-m+|n_3|)}\end{cases}+\cdots,$$
$$k=|q'-q| \tag{59}$$

(the upper sign and row apply to $q'>q$), integrals of type

$$\int_{4v}^{\infty}e^{-u}u^{|n_3|}L_{q+|n_3|}^{|n_3|}(u)\,L_{q'+|n_3|}^{|n_3|}(u)\,du$$

were neglected. The number of the nodes of Φ is the same at $v=0$ and $v\to\infty$ if

$$q=(l-|n_3|-p)/2. \tag{60}$$

We note here the asymptotic degeneration of the even (odd) Φ_l and odd (even) Φ_{l+1} to a common solution with $L_{q+|n_3|}^{|n_3|}(u)$ in expression (50) according to (60).

5.1.4. Because of the irregular singularity of (27) in the asymptotic range $r \to \infty$ the type of the asymptotic solutions could be explored only. By introducing $x = r^{-1}$ and using (58), (59) we find

$$B_{qq'} = B_{qq'}^{(\tilde{q})} x^{\tilde{q}} + \cdots \tag{61}$$

if $q \neq q'$,

$$A_{qq'} = A_{qq'}^{(\hat{q})} x^{\hat{q}} + \cdots, \tag{62}$$

where

$$\tilde{q} = 2\,|q - q'| - 1,$$
$$\hat{q} = 2\,|q - q'| - 2 + 4\,\delta_{qq'} + 2(\delta_{q,q'-1} + \delta_{q,q'+1}),$$

and (27) takes the form

$$x^4 f_q'' + [2E^* + 2Zx - (v^2 - \mu_q)\,x^2 + A_{qq}]\,f_q + \sum_{q'}{}' [A_{qq'} f_{q'} - B_{qq'} x^2 f_{q'}'] = 0. \tag{63}$$

Our main observation is that by (56), (59), (62),

$$2E^* + 2Zx + (\mu_q - v^2)\,x^2 + A_{qq} = -\kappa_q^2 + 2Zx + O(x^4), \tag{64}$$

where $\kappa_q = [-2E^* + 2(2q + |n_3| + 1)\omega]^{1/2}$. In (64) the term $-v^2x^2 = -\omega^2/x^2$ was cancelled; consequently the asymptotic behaviour of f_q at $x = 0$ is not determined by an equation of type

$$x^4 f_q'' - \omega^2 x^{-2} f_q = 0 \tag{65}$$

which would have provided a common asymptotic vanishing of type

$$f_q \propto \exp\{-\omega/(2x^2)\} \tag{66}$$

for any q. Rather, we have

$$f_q = \exp\{-\kappa/x\}\, v_q(x) \tag{67}$$

with a common κ. We can assume, e.g.,

$$v_q = \sum_{m=0}^{\infty} c_m^{(q)} x^{\gamma_q + m}; \tag{68}$$

we have, however, to bear in mind that (68) is not the most general form. (Equations (67) and (68) represent a special form of the general solution

$$f_q = \sum_{m=-\infty}^{\infty} c_m^{(q)} x^{\gamma + m} \tag{69}$$

which is very inconvenient to an eventual analytical analysis. An analytical method has not been found to determine (69) at $x \approx 0$.)

On using (61), (62), (67), and (68) in (63) we can determine κ, γ_q, and some coefficients $c_m^{(q)}$ if

$$\sum_{m=0}^{\infty} c_m^{(q)} x^{\gamma_q + m} \{\kappa^2 - \kappa_q^2 + 2x[Z + \kappa(\gamma_q + m - 1)] + x^2(\gamma_q + m)(\gamma_q + m - 1)\} + \sum_{q'}{}' \Big\{ [A_{qq'}^{(\hat{q})} x^{\hat{q}} + \cdots] \sum_{m=0}^{\infty} c_m^{(q')} x^{\gamma_{q'} + m} - [B_{qq'}^{(\tilde{q})} x^{\tilde{q}} + \cdots] \sum_{m=0}^{\infty} [\kappa c_m^{(q')} x^{\gamma_{q'} + m} + (\gamma_{q'}' + m)\, c_m^{(q')} x^{\gamma_{q'} + m + 1}] \Big\} = 0 \tag{70}$$

is solved for $x \ll 1$ by equating the coefficients of the different powers of x with 0. Two solutions have been found; these do not form the complete ensemble of the possible solutions.

Solution C. We choose a channel q^* as the dominant term at $x = 0$; $c_0^{(q^*)}$ is arbitrary,

$$\gamma_{q'} = \gamma_{q^* \pm k} = -\frac{Z}{\kappa} + k + 1 \tag{71}$$

$$c_1^{(q^*)} = \gamma_{q^*}(1 - \gamma_{q^*})\, c_0^{(q^*)}/2(Z + \kappa\gamma_{q^*}) \tag{72}$$

$$c_0^{(\bar{q}(k))} = \pm[(1 - \delta_{1k})\, A_{\bar{q}(k),\bar{q}(k-2)}^{(2)} c_0^{(\bar{q}(k-2))} - \kappa B_{\bar{q}(k),\bar{q}(k-1)}^{(1)} c_0^{\bar{q}(k-1)}]/(2k\omega), \qquad k = 1, 2, \ldots, \tag{73}$$

where

$$\bar{q}(k) = q^* \pm k,$$

and a little more complicated expression can be obtained for $c_1^{(q^* \pm 1)}$.

Solution D. We can choose

$$\kappa^2 \neq \kappa_q^2 \tag{74}$$

for any q which leads to

$$\gamma_q = \gamma_0 - q \tag{75}$$

$$c_0^{(q)} = (\kappa^2 - \kappa_{q-1}^2)\, c_0^{(q-1)}/\kappa B_{q-1,q}^{(1)}, \tag{76}$$

where $q = 1, 2, \ldots$, $c_0^{(0)}$ and γ_0 are arbitrary. This solution gives a divergent F at $x = 0$, as can be inferred from introducing it in (9).

5.1.5. From the computational point of view the result of our comprehensive asymptotic analysis is twofold. We have analytic expressions for $A_{ll'}$, $B_{ll'}$, μ_l in the asymptotic domains of ν, where their direct computation is not free of problems like loss of digits, lengthy iterations, and the amount of computing time.

We found the two types (the complete ensemble) of regular asymptotic solutions at $0 \leqslant r \ll 1$, at the regular singular point of (27) an one type at $x = 0$, in the irregular singularity of (27). Using them we can start the modified Numerov procedure very precisely. We are able to save many computing time since we have $f_l(r)$ or $f_q(x)$ for $r, x < m'h$, $m' \ll h^{-1}$ which ought to be found by many trial shootings otherwise. In many channel computations it was found namely that the resulting functions $f_l(r_s)$ or $f_q(x_s)$ were sensitive to the appropriate starting of the channel coefficients (i.e., to $df_{l'}/dr|_{r=0}$ $(l' = l, l \pm 2, ...)$ or $df_{q'}/dx|_{x=0}$ $(q' = q, q \pm 1, ...)$), in contrast to a single channel calculation in which the error in the first derivative of the unknown function disappears very quickly not far from the starting point [21].

5.2. The Computation of the Coupling Matrix Elements at Intermediate Values of ν

By the transformation

$$\Phi = (1 - \eta^2)^{|n_3|/2} \phi(\eta, \nu) \tag{77}$$

(28) takes the form

$$(1 - \eta^2) \frac{\partial^2 \phi}{\partial \eta^2} - 2(|n_3| + 1)\, \eta \frac{\partial \phi}{\partial \eta} - [|n_3|\, (|n_3| + 1) - \nu^2 \eta^2 + \mu(\nu)]\, \phi = 0. \tag{78}$$

The series expansion of the solutions to (78),

$$\phi = \sum_{m=0}^{\infty} c_m(\nu)\, \eta^{2m+p}, \tag{79}$$

can be found by introducing assumption (79) in (78) and equating the different powers of η to zero from which the recurrence relation is obtained for c_m,

$$\nu^{-2} v_{m+1} c_{m+1} - w_m c_m + \nu^2 c_{m-1} = 0, \qquad m = 0, 1, 2, ..., c_{-1} = 0, \tag{80}$$

where

$$v_m = 2m(2m + 2p - 1)\nu^2$$

$$w_m = (2m + |n_3| + 1)(2m + 2p + |n_3|) + \mu.$$

Equations (80) represent a system of homogeneous linear equations which has a non-trivial solution if and only if its determinant vanishes. This condition is satisfied by a special $\mu(\nu)$ function given by the solutions of the equation as

$$w_0 - \frac{v_1}{w_1 -} \frac{v_2}{w_2 -} \cdots = 0. \tag{81}$$

Proof for the convergence of series (79) and details of the procedure sketched in (77)–(81) were given in [18].

A FORTRAN program was written to solve (81) by the series expansion technique of continued fractions described in [19]. The function $\mu_m(\nu)$—the mth root of (81)—was computed from the form

$$-\frac{v_{m-1}}{w_{m-2} -} \cdots \frac{v_1}{w_0} + w_{m-1} - \frac{v_m}{w_m -} \frac{v_{m+1}}{w_{m+1} -} \cdots = t(\mu, \nu) = 0. \tag{82}$$

At a fixed value of ν μ was varied and the root was determined by an accuracy $|\delta\mu/\mu| < 10^{-12}$. The length of the second continued fraction in (82) was increased until the relative accuracy of $t(\mu, \nu)$ reached 5% (at $t(\mu, \nu) \approx 0$ as well). Loss of digits during the computation of the continued fraction was carefully controlled. The numerical value of $\mu(\nu)$ was used in the numerical solution of (27) in the interval ν in which asymptotic formula (34) or (56) failed to give a prescribed accuracy (usually 10^{-11}). At $\nu \gg 1$ it was useful from the computational point of view to rearrange (82) by shifting m to higher values (e.g., to $m + 5$ at $\nu \approx 50$). A few $\mu(\nu)$ functions are drawn in Fig. 1.

In a subsequent FORTRAN program the normalized functions $\Phi_l(\nu, \eta)$ were computed by using (77), (79), (80)

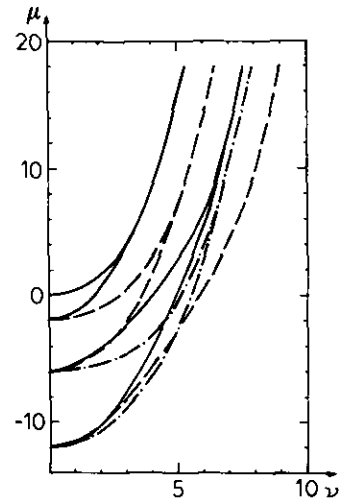

FIG. 1. A few $\mu(\nu)$ functions. Drawn line: $n_3 = 0$, dashed line $n_3 = 1$, dotted line $n_3 = 2$.

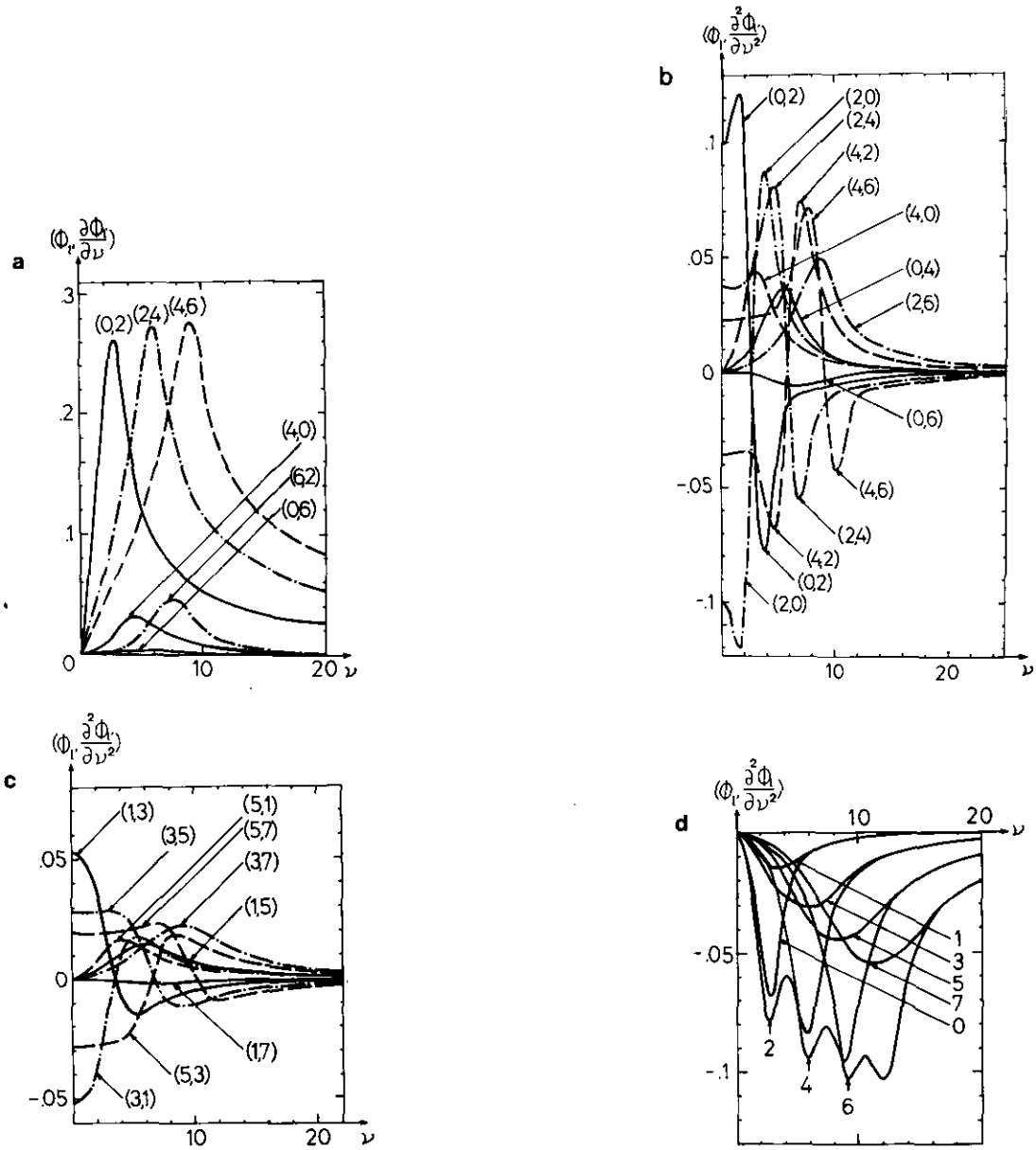

FIG. 2. A few matrix elements for $n_3 = 0$. The curves are labelled by the value of l if $r = 0$.

with the $\mu(\nu)$ determined according to the preceding paragraph. For (16) $\partial\Phi_l/\partial\nu$ was computed by numerical differentiation of the coefficients c_m of expansion (79) by a midpoint formula. (Using this $\partial\Phi_l/\partial\nu$ the accuracy of satisfying (30) was controlled; typically $|B_{ll}| < 10^{-8}$ was found numerically. If $l \neq l'$ by deriving (29) twice we find a check again which consists of integrals over the products of Φ_l and $\partial\Phi_{l'}/\partial\nu$ if (16) is used. For this zero result $10^{-9} - 10^{-11}$ was found in the computations.) In order to be able to interpolate $A_{ll'}, B_{ll'}$ the coupling matrix elements were computed by an accuracy 10^{-6} to a grid of ν points in the intermediate range of ν, the distance of the grid points was $\Delta\nu = 0.01$ at $\nu < 6$ and it was increased to $\Delta\nu = 0.1$ at $\nu > 30$. In the interval $\nu < 0.01$ and $\nu > 40$ the asymptotic formulae (36), (37) and (58), (59) were used, respectively. For orientation a few matrix elements are drawn in Fig. 2 if $n_3 = 0$. The $n_3 = 1, 2, \ldots$ families of the matrix elements show similar morphology if they are arranged according to the number of the nodes of Φ.

In our problem the coupling matrix elements do not have singularity at all (this is not a general feature of problems of type (1)); they vanish at $r = 0$ and $r \to \infty$ as well. In the diagonal part of Eqs. (27) $-(A_{ll} + (\mu_l - \nu^2)/r^2)$ is an additional potential to the Coulomb one. It is a remarkable feature of this potential and of the coupling matrix elements that they are non-monotonous in the whole interval

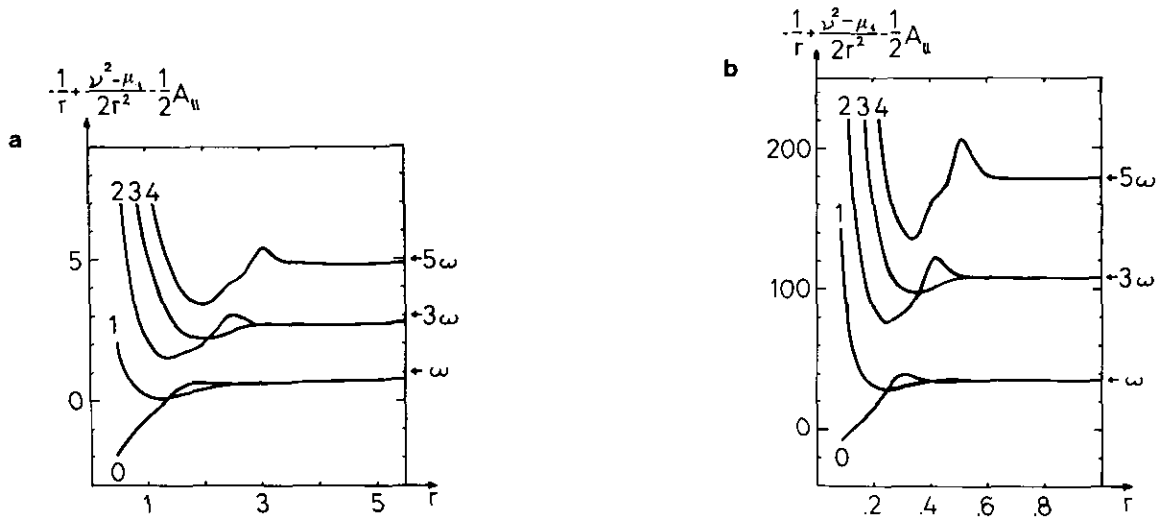

FIG. 3. A few adiabatic potentials for $n_3 = 0$ at $\omega = 1$ and $\omega = 36$.

$0 \leqslant r \leqslant \infty$ but they have inflexions and minima or maxima. A plot the adiabatic potentials shows that corresponding to the maximal value of $(\Phi_l, \partial^2\Phi_l/\partial\nu^2)$ an additional repulsive core appears at a fixed value of r $(r > 0)$ (see Figs. 3). With increasing ω it strengthens and gets closer to $r = 0$, the maxima even exceed the threshold value ($\kappa_q = 0$ in (64)) if ω is large. The accompanying minima correspond to quasi equilibrium positions for the electron. Beyond these regions the adiabatic potentials become Coulombic rapidly.

Since with increasing $|l - l'|$ the non-diagonal elements of $A_{ll'}$, $B_{ll'}$ vanish more and more rapidly in both asymptotic domains and their order of magnitude differences are present in the intermediate range as well Eqs. (27) are rather loosely coupled to each other. This is a good omen for the numerical solution; we can expect a high accuracy in E or ψ from a few channels.

5.3. The Numerical Integration

The coupled channel equations were solved by the modified Numerov procedure according to Section 4.3. The limits (r_s or x_s) of the integrations were fixed by the requirement that $E(r_s)$ or $E(x_s)$ be stable in the sixth figure.

5.3.1. Outward integration. First the limits E_l and E_u on E, $(E_l < E < E_u)$ were estimated, next by following the estimation of the relative error/step

$$T_m^{(\alpha)} = \frac{h^6 v_m^{(\alpha)VI}}{240 v_m^{(\alpha)}} \approx \frac{h^6}{240} w_m^{(\alpha)3} \tag{83}$$

[14], a grid of the points r was determined in a manner that $|T_m^{(\alpha)}| < 10^{-6}$ was for E_l and E_u as well in any grid point m and for all channels α. Except for E and f_l the value of all symbols in (27) were stored for the points of the grid in a suitable form to avoid superfluous additions.

Since at $0 \leqslant r = m'h \ll 1$,

$$|T_{m'}^{(l)}| \approx \frac{[l(l+1)]^3}{240 m'^6} \tag{84}$$

is independent of h our asymptotic expansions (38), (43)–(48) were used at $m' < 5$ as indicated in Section 4.3 to bridge over the critical region where $|T_{m'}^{(l)}| > 10^{-6}$ holds, the subroutine was switched off which changed h.

The solutions were parametrized at a fixed value of ω: an adiabatic approximation and Solution B have E as an undetermined parameter only while Solution A has the ratios $c_0^{(l)}/c_0^{(l+2)}$ etc. as parameters. By iterating for them we have to find the solutions which show up correct asymptotic behaviour at $r \to \infty$. The two asymptotic solutions are of completely different type at $r \approx 0$. The undetermined coefficient $c_0^{(l)}$ is the normalization factor in A and B as well.

Table I is a summary of some results in the subspace magnetic quantum number $n_3 = 0$, even parity; we compare our results to the extensive material published in [2]. It is remarkable that the relative error of the two-channel calculation for the ground state has a vanishing trend outside the strong mixing ($\omega \approx 10$), at high field strength as well as at small field strength. For the state $1s\sigma$ the high field limit of the computations is where the functions $f_l(r_s)$ became a noisy function of E: E was changed, e.g., by 10^{-10} or 10^{-15} while $f_l(r_s) \approx 0$ oscillated randomly on a scale $|f_l(r_s)/\max(|f_l(r)|)| \approx 10^{-2} - 10^{-4}$, $0 \leqslant r \leqslant r_s$, $l = 0, 2, \ldots$. The instability was found in more than one-channel integrations only; with increasing the number of the channels and field strength ω it became more and more serious. Its most

TABLE I

The Eigenvalues E of the Levels $1s\sigma$ and $10s\sigma$ of a Hydrogen Atom in the Homogeneous Magnetic Field **H**

ω	$E_{[2]}$	E	$f^2_{\langle 1\rangle}$	$f^2_{\langle 2\rangle}$	$f^2_{\langle 3\rangle}$	$f^2_{\langle 4\rangle}$	r_s
0.01	−0.499900; 2	−0.499902	1.000				12
0.03	−0.499104; 2	−0.499101	1.000				11
		−0.499105	0.999992	0.000008			12
0.07	−0.495198; 3	−0.495096	1.000				10
		−0.495199	0.99981	0.00019			10
0.3	−0.427463; 7	−0.421702	1.000				9
		−0.427330	0.9954	0.0046			9
		−0.427460	0.99496	0.00496	0.00008		9
1.0	−0.022214; 11	−0.022121	0.9876	0.012	0.0004		8
		−0.022206	0.9877	0.0118	0.0004	0.00001	8
7.0	5.03879; 21	5.06793	0.988	0.012			5
		5.04101	0.9862	0.0129	0.0009		4
150.0	144.639; 12	147.850	1.000				1.5
		145.277	0.994	0.006			1.5
10^{-5}		−0.00499916	1.000				330
		−0.00499890	0.6687	0.3313			320
		−0.00499885	0.5405	0.3783	0.0812		320
		−0.00499885	0.5137	0.3765	0.1006	0.0276	320
5×10^{-5}		−0.00497651	1.000				320
		−0.00497278	0.5673	0.4327			320
		−0.00497164	0.4479	0.4572	0.0948		320
		−0.00497148	0.4239	0.4494	0.1151	0.0116	320
10^{-4}		−0.00491450	1.000				320
		−0.00488917	0.3389	0.6611			320
		−0.00488788	0.2605	0.5934	0.1462		320
		−0.00488739	0.2466	0.5748	0.1632	0.0154	320

Note. $E_{[2]}$ is taken from [2]; it is followed by the number of channels in Legendre or Landau basis. The number of the steps in the numerical integration did not exceed 600.

likely interpretation is that the coupling matrix elements were noisy in the seventh etc. figures and this noise was amplified during the numerical integration. The instability and the enormous digit loss is under study; they become pronounced in the region of strong mixing and are probably connected to the physical nature of the problem. For the state $10s\sigma$ the high field limit is where the accuracy of E in the four-channel calculation is less than six figures.

Table I shows that if the angular oblate functions are used as a basis the necessary number of channels is reduced to ca half compared to that of the Legendre basis. The Schrödinger eqution of a hydrogen atom in strong magnetic field can be solved by the Born expansion method if cylindrical coordinates are used. From the excellent agreement of the computed eigenvalues by the adiabatic solution—the upper-lower theorem was applied in [20]—and by a many (≈ 10) channel calculation in a Landau basis at the high field limit we can infer that a 2–3-channel calculation using the Born expansion method gives roughly the same accuracy as the 10-channel calculation in the Landau basis [2].

The solutions of type B were found at discrete values of ω only where $c_0^{(l)}(\omega)=0$ was in a solution of type A; e.g., in a two-channel computation for the state $3s\sigma$ $c_0^{(0)}=0$ was at $\omega=0.0428052$, $E=0.0002598$ and $c_0^{(2)}=0$ was at $\omega=0.16714$, $E=0.13072$.

5.3.2. The inward integration was performed for Solution C only because this solution was promissory of saving computing time if compared to the needs of Solution A: many shootings could have been saved because there was no need to iterate for the parameters c_2/c_0 etc.

The relative error/step was estimated from (67) directly:

$$T^{(q)}_{m'} \approx \frac{\kappa^6}{240h^6m'^{12}}. \tag{85}$$

$T^{(q)}_{m'}=10^{-6}$ was taken in (85), (67) was used for $x\leqslant (m'+5)h$, while (20) was applied for the actual integration of (63) if $x>(m'+5)h$. At $x\to\infty$, $f_q(x_s)\to 0$ was searched for the channels $l\neq 0$, and h could be increased rapidly because $T^{(q)}_m \propto h^6x_m^{-12}$; stable $E(x_s)$ was found from a moderate number of steps. The expected behaviour,

$$f_l \propto x^{-l}, \tag{86}$$

TABLE II

Some Results from the Outward and Inward Integration at $\omega = 0.001$, for the States $3d\sigma$ and $3s\sigma$

E	$h_{\min}$	$h_{\max}$	m^*	r_s	c_0^{-1}	c_2^{-1}	$f^2_{\langle 0\rangle}$	$f^2_{\langle 2\rangle}$
(outward)								
−0.0555254	0.01	0.32	206	50		110.8		1
−0.0555349	0.01	0.32	209	50	−6.46	119.6	0.162	0.838
−0.0554862	0.01	0.32	209	50	2.59		1	
−0.0554773	0.001	0.256	275	50	2.83	0.0283	0.837	0.163
(inward)				x_s	l			
−0.0555412	10^{-3}	0.256	308	40	≈10			
−0.0555264	10^{-4}	0.4096	492	35	≈8			
−0.0555255	10^{-4}	0.4096	646	30	≈4			

Note. $E = -0.0555349$ and -0.0554774 are given from a three-channel computation in [2], m^* is the number of the steps of our integrations, $|T_m^{(l)}| = |T_m^{(q)}| = 10^{-6}$ was except for the last line, where $|T_m^{(q)}| = 10^{-8}$ was, the values of c_l ($l = 0$ or 2) normalize (26) to unity.

where $l = 2q + |n_3| + p$, was not found, even in adiabatic calculations. The failure to find (86) was caused by cummulative errors and insufficient accuracy of our computations. The eigenvalues from the inward and outward integrations were in agreement only in adiabatic calculations. This result is a verification of the second point in Section 5.1.5 by means of computations; the adiabatic results are insensitive to the starting while this is not true for the non-adiabatic results. Finally we mention that the inward integration gave the same precision in E if h and $|T_m^{(q)}|$ were smaller, compared to the outward integration; i.e., the inward integration needed more computing time. This finding could be anticipated from comparing (27) and (63). Table II reports some results.

6. CONCLUSIONS

A Born expansion method was reviewed and elaborated in detail for non-separable quantum mechanical eigenvalue problems. It was indicated in general terms how to determine asymptotic expansions of the coupling matrix elements and diagonal potentials.

By purely analytical and algebraic considerations in one of the singular points of our problem (in the regular singularity on the axis x) all regular solutions were constructed and they could be mapped in a very natural way. It was sketched how an initial value of the wave function can be calculated in a singular point so as to be able to start a numerical integration from this point.

Our procedure has the advantages compared to more conventional procedures (perturbative or variational treatment or diagonalization techniques in a basis which does not fit the problem optimally) as follows:

— analyticity, consequently clarity, at least in one of the singular points

— our basis functions constitute a basis to expand F in wich we are able to make a lucid distinction whether a problem itself is integrable or not. The choice of more ad hoc bases to expand F can, namely, lead to numerical and computational troubles in some domains of the spectrum E where the problem (1) itself is perhaps fully regular.

The Numerov procedure was fitted to our coupled system of second-order ordinary differential equations which contained originally first derivatives of the unknown functions in the coupling terms.

The asymptotic analysis and some numerical results concerning the Schrödinger equation of a hydrogen atom in a strong homogeneous magnetic field were included which gave an impression of the usefulness of our method. The numerical results show that the Born expansion method is a viable alternative for computational applications which leads to a reduction of computing efforts, compared to an eigenfunction expansion in a Legendre or Landau basis.

All computations could be performed by an IBM-compatible PC: two smaller FORTRAN programmes (composed of ca 300–400 statements) gave $\mu(v)$ and the matrix elements while the numerical integration was performed by a program of a length of ca 1200 statements. Computing times are of relative value if PCs are used; we mention that the four-channel computation of Solution A (an accuracy 10^{-6}in E at $\omega = 1.0$) needed some hours.

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