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'PERTURBATION METHODS IN QUANTUM MECHANICS

by

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ABSTRACT

The solutions of the radial part of the Schrödinger equation for the hydrogen atom, which may be written (in atomic units) as

$$\left\{ -\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} - \frac{2}{r} \right\} \Psi(r) = E \Psi(r)$$

are well known in the standard case when the boundary conditions require that the wave function should vanish for infinite r . The eigenfunctions in this case are expressible in terms of Laguerre polynomials and the eigenvalues of the energy are

$$E_n = -\frac{1}{n^2} \quad (n = 1, 2 \dots)$$

The problem of determining the eigenvalues when the boundary conditions require that Ψ should vanish for a finite r , say r_0 , is not as amenable to solution, and it is only recently that several methods have been suggested for dealing with this case. The method to be discussed here is due to Michels, de Boer, and Bijl. De Boer, considering the ground state alone, succeeds through the use of a perturbation method in finding the change in the eigenvalues for different r_0 . In so doing, he makes an approximation, which a priori is not justified. In the present thesis, it is shown both qualitatively and quantitatively that the approximation is justified for the values of r_0 used. The logical extension of the method to states other than the ground state is made for two particular cases, and from the results of these two investigations, conclusions are drawn regarding the general applicability of de Boer's method.

INTRODUCTION

One of the most interesting facets of Quantum Mechanics to a mathematician is the set of methods developed therein for finding approximate solutions to differential equations, the exact solutions of which cannot be found. These "perturbation" methods have had to be developed by the physicist since the number of problems for which the corresponding Schrödinger equation is capable of exact solution is relatively small. The standard problems in the last mentioned class lead to a study of the Legendre, Hermite, Laguerre, and Bessel functions -- and as these names indicate, the required mathematics was developed long before the advent of Quantum Mechanics. But for many other problems (for example, the problem of determining the interaction between an atom and a radiation field) a new mathematical technique has to be developed. The usual approach for many of these perturbed eigenvalue problems is the following [3, pp. 149 et. seq.].

The Schrodinger equation for the stationary state is $H\Psi = W\Psi$ where

$$H = - \frac{\hbar^2}{2m} \nabla^2 + V .$$

It is assumed that H may be written as the sum of two parts for one of which, say H_0 , the solution of the Schrödinger equation is known. Let the other part, H' , be small enough to be regarded as a perturbation on H_0 . Let the eigenfunctions and

eigenvalues to H_0 be u_n and E_n respectively. That is, $H = H_0 + H'$ and $H_0 u_n = E_n u_n$. Ψ and W are then expanded in power series in terms of a parameter λ as follows:

$$\begin{aligned}\Psi &= \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots \\ W &= W_0 + \lambda W_1 + \lambda^2 W_2 + \dots\end{aligned}$$

Substituting these values into the wave equation,

$$(H_0 + \lambda H')(\Psi_0 + \lambda \Psi_1 + \dots) = (W_0 + \lambda W_1 + \dots)(\Psi_0 + \lambda \Psi_1 + \dots)$$

where H' has been replaced by $\lambda H'$, where λ will finally be replaced by 1. Equating coefficients of equal powers of λ on each side of this equation leads to a system of equations giving successively higher orders of the perturbation.

$$\begin{aligned}H_0 \Psi_0 &= W_0 \Psi_0 \\ H_0 \Psi_1 + H' \Psi_0 &= W_0 \Psi_1 + W_1 \Psi_0 \\ H_0 \Psi_2 + H' \Psi_1 &= W_0 \Psi_2 + W_1 \Psi_1 + W_2 \Psi_0 \text{ etc.}\end{aligned}$$

From the first of these, it follows that Ψ_0 is one of the u_n 's. Solving the second of this series of equations with Ψ_0 replaced by u_m will give the first order solution. The solutions to higher order in H' are found from the succeeding equations.

The above perturbation method has proved satisfactory especially since the perturbing terms (i.e., the interaction terms) are, in practice, very small. But there is another class of problems for which this direct method does not work. In this latter type of problem, the perturbation due to a confinement of the quantum mechanical system is to be found. The resulting changes in the eigenvalues would appear as shifts in the spectral lines of

atoms under pressure or in a crystal and the resulting changes in the eigenfunctions might show up, for example, in the rate of radioactivity of an atom under pressure.

Mathematically, these problems can be formulated in the following way: find the eigenfunctions and eigenvalues of $H \Psi = E \Psi$ where Ψ must vanish at the ends of an interval, the interval being smaller than the usual range of the independent variable. For example, for the problem discussed in the body of the thesis, the solution of Laguerre's equation which vanishes at 0 and r_0 , where $r_0 < \infty$, is required.

It is possible that this latter perturbation problem can be reduced to one of the first type mentioned but so far this idea has not been completely worked out. Meanwhile, however, several other attempts have been made to solve bounded eigenvalue problems. The best known of these, and the most general, is the graphical method of Sommerfield [4], it is limited in its accuracy and moreover gives no information about the eigenfunctions. A second method, which will be discussed below is due to Michels, de Boer, and Bijl [2]. A third method, due to Auluck and Kothari [1], makes use of asymptotic series.

1. THE GROUND STATE

1.1. An Outline of the De Boer Method

The Schrödinger equation for a hydrogen atom, in terms of spherical polar coordinates, is

$$-\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial}{\partial \rho} + \frac{\Omega}{\rho^2} \right] \mu - \frac{Ze^2}{\rho} \mu = H \mu \quad (1)$$

where $\Omega = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}$,

μ is the reduced mass and H is the energy in ergs.

By a separation of variables, the radial part of the wave equation for $\Psi(\rho)$

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{1}{\rho^2} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \frac{Ze^2}{\rho} + \frac{l(l+1)\hbar^2}{2\mu\rho^2} \right\} \Psi(\rho) = H \Psi(\rho) \quad (2)$$

is obtained. This is the only equation that need by used here, since the new boundary condition of this problem can involve a change only in the radial part of the wave function. Equation (2) may be written in dimensionless form by introducing two dimensionless variables r and E with $r = \alpha\rho$, $E = H/H_0$ where

$$\alpha = \frac{Ze^2\mu}{\hbar^2}, \quad H_0 = \frac{\hbar^2\alpha^2}{2\mu}$$

This substitution leads to the equation

$$\left\{ -\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{r^2} - \frac{2}{r} \right\} \Psi(r) = E \Psi(r) \quad (3)$$

The method of solution given by de Boer [2] will now be outlined.

To solve equation (3), Sommerfeld's polynomial method is used. Let

$$\Psi(r) = \frac{1}{r} e^{-\frac{r}{a}} f(r), \quad a = \sqrt{\frac{1}{E}} \quad (4)$$

and then (3) gives the equation

$$\left\{ \frac{d^2}{dr^2} - \frac{2}{a} \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2}{r} \right\} f(r) = 0 \quad (5)$$

for determining the polynomial $f(r)$. Writing $f(r) = \sum c_s r^s$ leads to the recursion formula

$$c_s \{s(s-1) - l(l+1)\} = c_{s-1} \left\{ 2 \frac{s-1}{a} - 2 \right\} \quad (6)$$

The smallest value of s that occurs must therefore satisfy

$$s(s-1) = l(l+1); \text{ i.e., either } s = -l \text{ or } s = l+1.$$

From the first boundary condition, that $\frac{1}{r} f(r)$ must be finite at $r = 0$, the value $s = l+1$ must be chosen. In the unbounded problem, the second boundary condition is that the wave function should vanish for infinite r and this is satisfied if the power series terminates. It follows from (6) that if the series is to terminate, then the highest power n of r that occurs must satisfy

$$\frac{2n}{a} - 2 = 0$$

i.e. $n = a$ (7)

Thus the eigenvalues of E , by (4), are

$$E = -1/n^2 \quad (8)$$

However, the second boundary condition in the problem considered here is that the wave function shall vanish at a finite r equal, say, to r_0 . This condition is that

$$f(r_0) = \sum_{l+1}^{\infty} b_s r_0^s = 0 \quad (9)$$

De Boer now proceeds to treat the ground state ($l = 0, n = 1$) only, by taking for the unperturbed case $a = 1, E = -1$; and for the perturbed case, letting

$$a = 1 + \beta \quad E = -\frac{1}{(1+\beta)^2} \sim -1 + 2\beta \quad (10)$$

Substituting these values into (6) gives

$$b_s s(s-1) = b_{s-1} 2 \frac{s-2-\beta}{1+\beta}$$

which, neglecting β against 1, leads to

$$b_1 = 1, \quad b_s = \frac{-2^{s-1} \beta}{(s-1) s!} \quad (11)$$

The wave function can then be written as

$$\Psi(r) = e^{-\frac{r}{1+\beta}} \left\{ 1 - \beta \sum_2^{\infty} b'_s r^{s-1} \right\} \quad (12)$$

with $b_s = -\beta b'_s$.

Then from (9) the value of β can be obtained as

$$\beta = \frac{1}{\sum_2^{\infty} b'_s r_0^{s-1}} \quad (13)$$

where b'_s is independent of β .

A set of values of $\Delta E \sim 2\beta$ are given:

ρ	r_0	$\beta \times 10^3$	ΔE in e.v.
$5a_0$	5	3.45	.0927
$6a_0$	6	.727	.0196
$7a_0$	7	.1383	.00375
$8a_0$	8	.0257	.00069

$a = \frac{\hbar^2}{\mu e^2 Z}$ is the radius of the first Bohr orbit.

This completes the resume of [2].

1.2 Uniform Convergence of the Series

Upon study of this paper, the question arises whether the approximation used in arriving at the expression (11) for the coefficients b_s is valid. This approximation tacitly assumes that for s large, the contribution of the s th term is so small

that the error introduced by replacing $(1 + \beta)^{s-1}$ by 1 is negligible. This assumption will now be justified, firstly, by a qualitative approach which will lead to the conclusion that for β "small enough" the approximation can indeed be made; secondly, by a more quantitative approach whereby an actual range for the true value of β will be obtained and an upper bound for the error introduced by the approximation calculated.

Let the exact series corresponding to the approximate series appearing in (12) be denoted by $\sum_2^{\infty} p_s r^{s-1}$ where

$$p_s = 2^{s-1} \frac{(s-2-\beta)(s-3-\beta) \dots (1-\beta)(-\beta)}{s! (s-1)! (1+\beta)^{s-1}}$$

Then

$$\begin{aligned} \sum_2^{\infty} p_s r^{s-1} &= \sum \frac{(s-2-\beta)(s-3-\beta) \dots (1-\beta)(-\beta)}{s! (s-1)!} \left(\frac{2r}{1+\beta}\right)^{s-1} \\ &= -\beta \left[\frac{1}{2!1!} \frac{2r}{1+\beta} + \frac{(1-\beta)}{3!2!} \left(\frac{2r}{1+\beta}\right)^2 + \frac{(2-\beta)(1-\beta)}{4!3!} \left(\frac{2r}{1+\beta}\right)^3 + \dots \right] \end{aligned}$$

To indicate the dependence of the series inside the bracket on β , call it $S(\beta)$. The corresponding approximate series is

$$S(0) = \frac{1}{2!1!} 2r + \frac{1}{3!2!} (2r)^2 + \frac{2!}{4!3!} (2r)^3 + \dots$$

If it can now be shown that $S(\beta)$ converges uniformly with respect to β , then the qualitative conclusion will follow, since $S(\beta)$ being uniformly convergent means that

$$|S_n(\beta) - S_N(\beta)| < \epsilon \quad \text{for all } n > \text{fixed } N(\epsilon),$$

where N is independent of β . Thus N can be chosen so that the remainder of the $S(\beta)$ series is as small as is desired for all β , and may therefore be neglected in the calculations. This leaves a finite number of terms in the $S(\beta)$ series,

each of which approaches the corresponding term in $S(0)$ as $\beta \rightarrow 0$. Therefore, for β small enough, the sum of the first N terms of $S(\beta)$ will be close enough to the sum of the first N terms of $S(0)$ to justify using $S(0)$ in the computations.

$S(\beta)$ converges uniformly by the Weierstrass M test, since if $2r < M$ and $0 \leq \beta < 1$, then

$$\frac{(s-2-\beta)(s-3-\beta)\cdots(1-\beta)}{s!(s-1)!} \left(\frac{2r}{1+\beta}\right)^{s-1} < \frac{M^{s-1}}{(s-1)s!}$$

The series whose s th term is $\frac{M^{s-1}}{(s-1)s!}$ is a convergent series of positive terms; hence $S(\beta)$ converges uniformly. This completes the qualitative argument.

1.3 An Upper Bound for the Error due to de Boer's Approximation

In order to obtain the range in which the true value of β lies and an upper bound to the error involved in using the approximation for the different values of r , consider first of all bounds for the expression

$$r + \sum_{s=2}^{\infty} \frac{(s-2-\beta)(s-3-\beta)\cdots(1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r^s \quad (14)$$

which is the exact expression for $f(r)$ corresponding to de Boer's value obtainable from (11).

Now

$$(14) \geq r + \sum_{s=2}^{\infty} \frac{2^{s-1}(-\beta)r^s}{s!(s-1)} = r - \beta \sum_{s=2}^{\infty} \frac{2^{s-1}r^s}{s!(s-1)} \quad (15)$$

Note that the right hand side of (15) is de Boer's $f(r)$.

$$\begin{aligned}
\text{Also } r + \sum_{s=2}^{\infty} \frac{(s-2-\beta)(s-3-\beta) \dots (1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r^s \\
= r - \frac{\beta}{1+\beta} r^2 + \sum_{s=3}^{\infty} \frac{(1-\frac{\beta}{s+2})(1-\frac{\beta}{s+3}) \dots (1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r^s \\
\leq r + \sum_{s=2}^{\infty} \frac{2^{s-1} (1-\beta)^{s-2} (-\beta)}{s!(s-1)!(1+\beta)^{s-1}} r^s \\
\leq r + \sum_{s=2}^{\infty} \frac{2^{s-1} (1-\beta)^{s-2} (1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} r^s \\
= r - \beta \sum_{s=2}^{\infty} \frac{r^s}{s!(s-1)} \left\{ 2 \frac{1-\beta}{1+\beta} \right\}^{s-1} \quad (16)
\end{aligned}$$

Combining (15) and (16):

$$\begin{aligned}
-\beta \sum_{s=2}^{\infty} \frac{2^{s-1} r^s}{s!(s-1)} \\
\leq \sum_{s=2}^{\infty} \frac{(s-2-\beta)(s-3-\beta) \dots (1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r^s \\
\leq -\beta \sum_{s=2}^{\infty} \frac{r^s}{s!(s-1)} \left\{ 2 \frac{1-\beta}{1+\beta} \right\}^{s-1} \quad (17)
\end{aligned}$$

From $e^{rt} = 1 + rt + \frac{(rt)^2}{2!} + \dots$ it follows that

$$-\beta \sum_{s=2}^{\infty} \frac{t^{s-2}}{s!} r^s = -\beta \frac{e^{rt} - rt - 1}{t^2} \quad (18)$$

and then

$$-\beta \sum_{s=2}^{\infty} \frac{t^{s-1} r^s}{s!(s-1)} = -\beta \int_0^t \frac{e^{ru} - ru - 1}{u^2} du \quad (19)$$

It is easily verified that the integral is convergent at the lower limit. Putting $\int_0^t \frac{e^{ru} - ru - 1}{u^2} du = F(t)$,

and noting that

$$\begin{aligned} 2 \frac{1-\beta}{1+\beta} &= 2(1-\beta)(1-\beta+\beta^2-\dots) \\ &= 2(1-2\beta+2\beta^2-\dots) > 2(1-2\beta) \end{aligned}$$

so $F\left(2\frac{1-\beta}{1+\beta}\right) > F(2-4\beta)$

(17) may then be written

$$-\beta F(2) \leq \text{Exact Series} \leq -\beta F\left(2\frac{1-\beta}{1+\beta}\right) \leq -\beta F(2-4\beta) \quad (20)$$

Rewriting,

$$-\beta \int_0^2 \frac{e^{ru} - ru - 1}{u^2} du \leq \text{Exact Series} \leq -\beta \int_0^{2-4\beta} \frac{e^{ru} - ru - 1}{u^2} du \quad (21)$$

Therefore, the maximum percentage error that can arise will be

$$\frac{\int_{2-4\beta}^2 \frac{e^{ru} - ru - 1}{u^2} du}{\int_0^2 \frac{e^{ru} - ru - 1}{u^2} du} \times 100\% \quad (22)$$

Thus, if an upper bound can be found for this expression, it will certainly also be an upper bound for the actual percentage error that occurs. To this end, it will be necessary to get approximations to the area under the curve

$$y = \frac{e^{ru} - ru - 1}{u^2}$$

It will be shown first that this curve is always concave upwards for $u \geq 0$.

$$\begin{aligned} \frac{dy}{du} &= \frac{u^2 \{r e^{ru} - r\} - \{e^{ru} - ru - 1\} 2u}{u^4} \\ &= \frac{e^{ru} \{ru - 2\} + ru + 2}{u^3} \end{aligned} \quad (23)$$

$$\begin{aligned} \frac{d^2y}{du^2} &= \frac{e^{ru} \{r^2 u^2 - 4ru + 6\} - 2ru - 6}{u^4} \\ &= \sum_{n=4}^{\infty} \frac{n^2 - 5n + 6}{n!} r^n u^{n-4} \end{aligned}$$

and, for $n \geq 4$, $\frac{n^2 - 5n + 6}{n!}$ is always positive since the two roots of $n^2 - 5n + 6$ occur at $n = 2$ and $n = 3$. Therefore, the second derivative being always positive for u positive, $y(u)$ will be concave upwards.

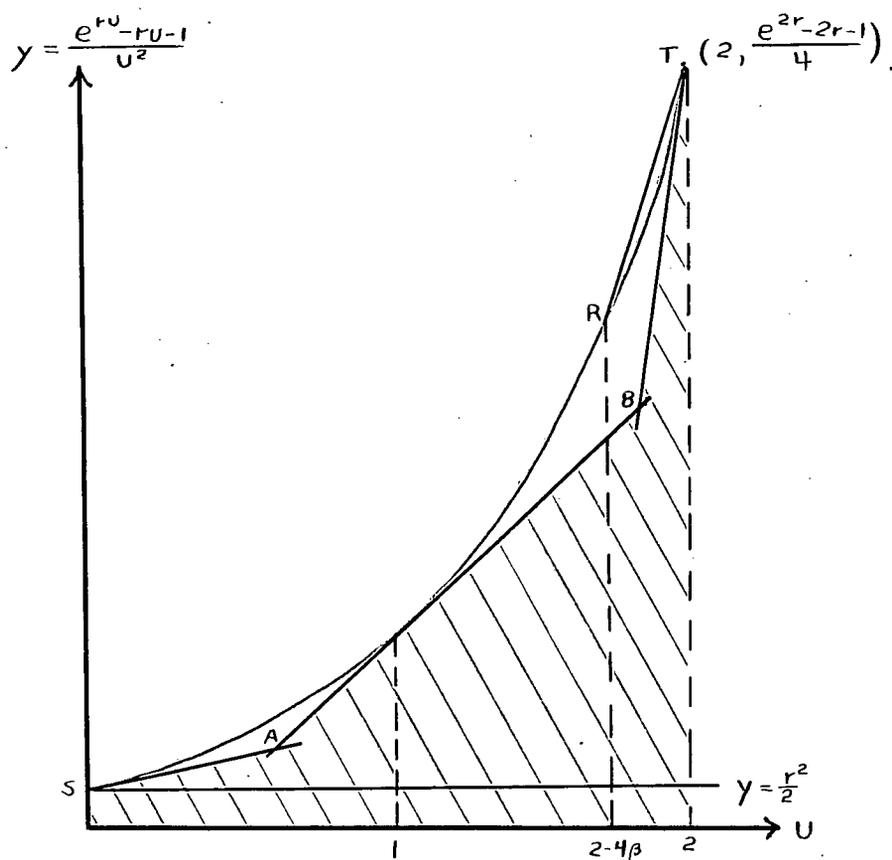


FIG. 1

An upper bound for (22) can now be obtained in the following manner. The denominator of (22) which is the area under $y(u)$ from $u = 0$ to $u = 2$ may be decreased by taking instead the shaded area shown in Figure 1. By elementary analytic geometry, the equations of the lines through SA, AB, and BT are

$$y = \frac{r^3}{6}u + \frac{r^2}{2} \quad (24)$$

$$y = \{e^r(r-2) + r + 2\}u + e^r(3-r) - 2r - 3 \quad (25)$$

$$y = \frac{e^{2r}(r-1) + r + 1}{4}u + \frac{e^{2r}(3-2r) - 4r - 3}{4} \quad (26)$$

respectively. The u coordinate of A, the point of intersection of (24) and (25) is

$$u_A = \frac{e^r(3-r) - 2r - 3 - \frac{r^2}{2}}{\frac{r^3}{6} - \{e^r(r-2) + r + 2\}} \quad (27)$$

The u coordinate of B, the point of intersection of (25) and (26) is

$$u_B = \frac{e^{2r}(2r-3) + 4e^r(3-r) - 4r - 9}{e^{2r}(r-1) - 4e^r(r-2) - 3r - 7} \quad (28)$$

Thus the shaded area of Figure 1 can be written

$$\int_0^{u_A} \left\{ \frac{r^3}{6}u + \frac{r^2}{2} \right\} du + \int_{u_A}^{u_B} \left\{ [e^r(r-2) + r + 2]u + e^r(3-r) - 2r - 3 \right\} du \\ + \int_{u_B}^2 \left\{ \frac{e^{2r}(r-1) + r + 1}{4}u + \frac{e^{2r}(3-2r) - 4r - 3}{4} \right\} du \quad (29)$$

The numerator of (22), which is the area under $y(u)$ from $u = 2 - 4\beta$ to $u = 2$ may be increased by taking instead the area of the trapezoid whose vertices are R, T, (2, 0), and $(2 - 4\beta, 0)$. This area is

$$2\beta \left\{ \frac{e^{2r} - 2r - 1}{4} + \frac{e^{r(2-4\beta)} - r(2-4\beta) - 1}{(2-4\beta)^2} \right\} \quad (30)$$

Thus the value of $\frac{(30)}{(29)} \times 100\%$ will be an upper bound for the error. A table of these values is given.

r_0	%error <
5	7.8
6	2.36
7	.47
8	.136

It may be concluded that for r_0 larger than 6, de Boer's method gives quite accurate results for the change in the eigenvalues. Note that in expression (30), which is used in calculating an upper bound for the error in β , β itself appears. That this fact does not seriously prejudice the calculations will be brought out more clearly in the following discussion, wherein a range for the true value of β will be found.

1.4. Determination of the Range for β .

Solving

$$r_0 + \sum_{s=2}^{\infty} \frac{(s-2-\beta)(s-3-\beta)\dots(1-\beta)(-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r_0^s = 0 \quad (31)$$

which is the exact $f(r)$ set equal to 0 for $r = r_0$, for β would give the true value of β . That is, one would like to solve

$$\beta \left\{ \frac{r_0^2}{1+\beta} + \sum_{s=3}^{\infty} \frac{(s-2-\beta)(s-3-\beta)\dots(1-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r_0^s \right\} = r_0 \quad (32)$$

Let the term inside the brackets in (32) be denoted by Σ .

Now, what de Boer does is to replace Σ by $\sum_{s=2}^{\infty} \frac{2^{s-1} r_0^s}{s!(s-1)}$ which is $> \Sigma$ (see (15)). Therefore, the value β_a

that he arrives at for β is actually smaller than the true one. De Boer's β_a will be used as the lower limit of the range for β .

To obtain a value of β larger than the true one, replace Σ by

$$\Sigma = \sum_{s=2}^{\infty} \frac{r^s}{s!(s-1)!} \left\{ 2 \frac{1-\beta}{1+\beta} \right\}^{s-1} \quad (33)$$

which is $< \Sigma$ (from (16)). But in solving for β from $\beta = r_0 / \Sigma$, de Boer's β_a has to be inserted in Σ and it might be that although $\Sigma(\beta) < \Sigma$, $\Sigma(\beta_a)$ is not $< \Sigma$, since β_a is smaller than the true value. It will next be shown that this difficulty can be avoided.

$$\begin{aligned} \beta \Sigma &= \beta \left\{ \frac{r_0^2}{1+\beta} + \sum_{s=3}^{\infty} \frac{(s-2-\beta)(s-3-\beta)\dots(1-\beta)}{s!(s-1)!(1+\beta)^{s-1}} 2^{s-1} r_0^s \right\} \\ &= \beta \frac{1-\beta}{(1+\beta)^2} \left\{ \frac{1+\beta}{1-\beta} r_0^2 + \frac{2^2 r_0^3}{3!2} + \frac{(1-\frac{\beta}{2}) 2^3 r_0^4}{4!3(1+\beta)} + \frac{(1-\frac{\beta}{3})(1-\frac{\beta}{2}) 2^4 r_0^5}{5!4(1+\beta)^2} + \dots \right\} \\ &> \beta \frac{1-\beta}{(1+\beta)^2} \left\{ \frac{1+\beta_a}{1-\beta_a} r_0^2 + \frac{2^2 r_0^3}{3!2} + \frac{(1-\beta_a) 2^3 r_0^4}{4!3(1+\beta_a)} + \frac{(1-\beta_a)^2 2^4 r_0^5}{5!4(1+\beta_a)^2} + \dots \right\} \end{aligned}$$

$$\text{since } \frac{1-\frac{\beta}{s-2}}{1+\beta} > \frac{1-\beta_a}{1+\beta_a} \quad \text{for } s \geq 4 \text{ if } \beta$$

is small.

$$\therefore \beta \Sigma > \beta \frac{1-\beta}{(1+\beta)^2} \sigma$$

where σ is the series involving β_a in the brackets above.

Now, from $\beta \frac{1-\beta}{(1+\beta)^2} \sigma = r_0$, it can be seen that the value of β obtained is actually too large, since σ is smaller than the corresponding exact series and β is the dominant term in the expansion of $\beta \frac{1-\beta}{(1+\beta)^2}$. Thus for an upper limit to the range of β , the smaller of the 2 values obtainable from the quadratic

$$\beta \frac{1-\beta}{(1+\beta)^2} \sigma = r_0$$

i.e.
$$\beta = \frac{\sigma - 2r_0 - \sqrt{\sigma^2 - 8r_0\sigma}}{2(\sigma + r_0)} \quad (34)$$

will be used.

Now
$$\sigma = \left\{ \frac{1+\beta_a}{1-\beta_a} \right\} \sum (\beta_a)$$

and from (18), (19), and (20),

$$\sum (\beta_a) = F\left(2 \frac{1-\beta_a}{1+\beta_a}\right) \geq F(2-4\beta_a) = \int_0^{2-4\beta_a} \frac{e^{rU} - rU - 1}{U^2} dU \quad (35)$$

But
$$\int_0^{2-4\beta_a} \frac{e^{rU} - rU - 1}{U^2} dU = \int_0^2 \frac{e^{rU} - rU - 1}{U^2} dU - \int_{2-4\beta_a}^2 \frac{e^{rU} - rU - 1}{U^2} dU$$

so a lower limit for

$$\int_0^{2-4\beta_a} \frac{e^{rU} - rU - 1}{U^2} dU$$

can be obtained by taking the lower bound found in (29) for

$$\int_0^2 \frac{e^{rU} - rU - 1}{U^2} dU$$

and subtracting from it the upper bound of

$$\int_{2-4\beta_a}^2 \frac{e^{rU} - rU - 1}{U^2} dU$$

found in (30). Then the value of β used as an upper limit

to the range of β is calculated here by solving (34) with

$\sigma' < \sigma$ in place of σ , where σ' is $\left\{ \frac{1+\beta_a}{1-\beta_a} \right\}^2$ times the

lower bound of $\int_0^{2-4\beta_a} \frac{e^{rU} - rU - 1}{U^2} dU$ mentioned above.

The range of β for the different r_0 's is tabulated below.

r_0	$< \text{True } \beta <$	
5	3.45×10^{-3}	24.7×10^{-3}
6	$.727 \times 10^{-3}$	1.27×10^{-3}
7	1.38×10^{-4}	1.84×10^{-4}
8	2.57×10^{-5}	9.5×10^{-5}

In finding each bound, two main approximations have been made. In each case, the first approximation was to replace the exact series by a simpler one; it would appear that this step cannot be avoided. The simpler series were then replaced by equivalent integrals, and the second approximations occurred in the numerical evaluation of these integrals. To be sure the last approximations were not too crude a check was made; for example, when an upper limit was required, a lower limit was also calculated and the difference between the two limits was compared to the range

$$\sum_{s=2}^{\infty} \frac{2^{s-1} r_0^s}{s!(s-1)!} - \sum_{s=2}^{\infty} \frac{2^{s-1} r_0^s}{s!(s-1)!}$$

In each case the difference was only a small fraction of this range and thus the error introduced by the second approximation, over which there is some control, was correspondingly small.

This completes the discussion of the ground state.

It is natural to inquire further and see if the method is applicable for states other than the ground state. First an s state with n different from 1, and then a typical p state, will be investigated. General conclusions concerning the applicability of the method will be drawn from the results of these investigations.

2. OTHER STATES

2.1 The s-State

Consider, then, the s state with $n = 2$. For the unperturbed atom, $a = 2$ and $E = -1/2^2$; therefore de Boer would take for the perturbed atom $a = 2 + \beta$ and

$$E = -\frac{1}{(2+\beta)^2} \sim -\frac{1}{4} + \frac{\beta}{4}$$

Substituting these values into (6) gives for the recurrence relation in this case

$$\begin{aligned} b_s s(s-1) &= b_{s-1} \left\{ 2 \frac{s-1}{2+\beta} - 2 \right\} \\ &= 2 b_{s-1} \frac{s-3-\beta}{2+\beta} \end{aligned} \quad (36)$$

which, neglecting β with respect to 2, leads to

$$b_1 = 1 \quad b_2 = -\frac{1}{2} - \frac{\beta}{4} \quad b_s = \frac{\beta}{s!(s-1)(s-2)} \quad (37)$$

($s \geq 3$)

The corresponding wave function is

$$\Psi(r) = e^{-\frac{r}{2+\beta}} \left\{ 1 - \left(\frac{1}{2} + \frac{\beta}{4}\right)r + \beta \sum_3^{\infty} b'_s r^{s-1} \right\} \quad (38)$$

with $b_s = \beta b'_s$

For this to vanish at $r = r_0$, β must be

$$\beta = \frac{\frac{1}{2} r_0 - 1}{\sum_3^{\infty} b'_s r_0^{s-1} - \frac{r_0}{4}} \quad (39)$$

Two values of β are given below

r_0	β
5	.59
10	.072

It may be remarked immediately that the value .59 for $r_0 = 5$ is certainly not small compared to 2 ; and thus one would expect a large error to arise from making the approximation that gives (37) . For $r_0 = 10$, however, the β is more reasonable.

2.2 An Upper Bound for the Error

An approximation to the upper bound for the error involved in this case will now be obtained in a manner analagous to that used previously. The exact expression this time for $f(r)$ is

$$r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (s-3-\beta) \dots (1-\beta)(-\beta)(-1-\beta) \beta r^s}{(2+\beta)^{s-1} s! (s-1)!} \quad (40)$$

$$= r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (s-3-\beta) \dots (2-\beta)(1-\beta^2) \beta r^s}{(2+\beta)^{s-1} s! (s-1)!}$$

$$\text{Now (40)} \leq r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (s-3)(s-4) \dots (1) \beta r^s}{2^{s-1} s! (s-1)!}$$

$$= r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \beta \sum_3^{\infty} \frac{r^s}{s! (s-1)(s-2)} \quad (41)$$

This would be de Boer's $f(r)$.

$$\text{Also } r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (s-3-\beta) \dots (1-\beta) \beta (1+\beta) r^s}{(2+\beta)^{s-1} s! (s-1)!}$$

$$= r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \frac{\beta(1+\beta)r^3}{3(2+\beta)^2} + \sum_4^{\infty} \frac{2^{s-1} \left(1 - \frac{\beta}{s-3}\right) \left(1 - \frac{\beta}{s-4}\right) \dots (1-\beta) \beta (1+\beta) r^s}{(2+\beta)^{s-1} s! (s-1)(s-2)}$$

$$\geq r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (1-\beta)^{s-3} \beta (1+\beta) r^s}{(2+\beta)^{s-1} s! (s-1)(s-2)}$$

$$\geq r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \sum_3^{\infty} \frac{2^{s-1} (1-\beta)^{s-1} \beta r^s}{(2+\beta)^{s-1} s! (s-1)(s-2)}$$

$$= r - \left(\frac{1}{2} + \frac{\beta}{4}\right) r^2 + \beta \sum_3^{\infty} \frac{r^s}{s! (s-1)(s-2)} \left\{ 2 \frac{1-\beta}{2+\beta} \right\}^{s-1} \quad (42)$$

Combining (41) and (42):

$$\begin{aligned} & \beta \sum_3^{\infty} \frac{r^s}{s!(s-1)(s-2)} \left\{ 2 \frac{1-\beta}{2+\beta} \right\}^{s-1} \\ & \leq \sum_3^{\infty} \frac{2^{s-1} (s-3-\beta) \dots (1-\beta)(-\beta)(-1-\beta) r^s}{(2+\beta)^{s-1} s!(s-1)!} \\ & \leq \beta \sum_3^{\infty} \frac{r^s}{s!(s-1)(s-2)} \end{aligned} \quad (43)$$

From the exponential series,

$$\beta \sum_3^{\infty} \frac{t^{s-3} r^s}{s!} = \beta \frac{e^{rt} - \frac{r^2 t^2}{2} - rt - 1}{t^3}$$

therefore, $\beta \sum_3^{\infty} \frac{t^{s-1} r^s}{s!(s-1)(s-2)} = \beta \int_0^t du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq \quad (44)$

Setting $\int_0^t du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq = G(t)$ and noting that

$$\begin{aligned} 2 \frac{1-\beta}{2+\beta} &= (1-\beta) \left(1 + \frac{\beta}{2}\right)^{-1} \\ &= (1-\beta) \left(1 - \frac{\beta}{2} + \frac{\beta^2}{4} \dots\right) \\ &= 1 - \frac{3}{2}\beta + \frac{3}{4}\beta^2 \dots \\ &> 1 - \frac{3}{2}\beta \end{aligned}$$

so $G\left(2 \frac{1-\beta}{2+\beta}\right) > G\left(1 - \frac{3}{2}\beta\right)$

(43) may then be written

$$\beta G\left(1 - \frac{3}{2}\beta\right) \leq \beta G\left(2 \frac{1-\beta}{2+\beta}\right) \leq \text{Exact Series} \leq \beta G(t) \quad (45)$$

Rewriting,

$$\beta \int_0^{1-\frac{3}{2}\beta} du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq \leq \text{Exact Series} \leq \beta \int_0^1 du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq \quad (46)$$

Thus, the maximum percentage error that can arise will be

$$\frac{\int_0^1 du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq}{\int_0^{1-\frac{3}{2}\beta} du \int_0^u \frac{e^{rq} - \frac{r^2 q^2}{2} - rq - 1}{q^3} dq} \times 100\% \quad (47)$$

To find an upper bound for this, which will be an upper bound for the error due to de Boer's approximation, it will be necessary to obtain an upper bound for the numerator of (47) and a lower bound for the denominator; so here again, approximate values of the integrals appearing are required. These can be obtained in the following way.

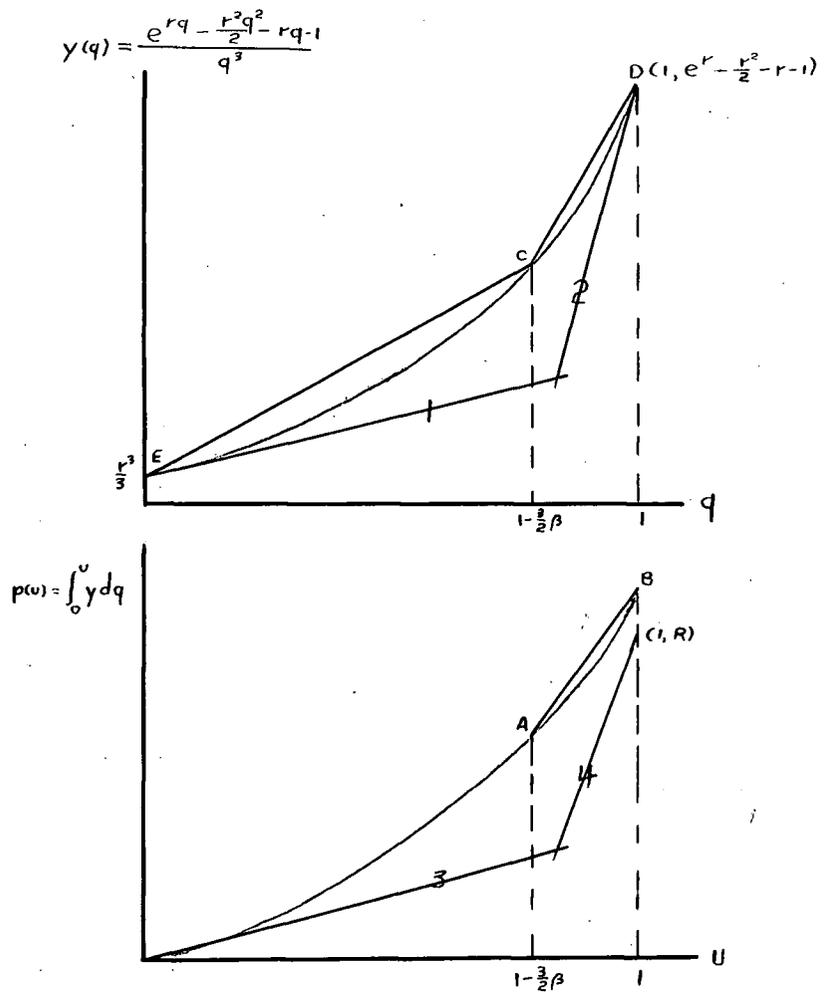


FIG 2.

Consider first the finding of an upper bound for the numerator of (47). The ordinate at any point in the lower diagram is the area up to that point in the top diagram. The area of the

trapezoid formed by A, B, $(1, 0)$, and $(1 - \frac{3}{2}\beta, 0)$ which one would like to use for the upper bound, will be increased by taking instead of the ordinate at A, the value obtained by taking the area of the trapezoid O, E, C, and $(1 - \frac{3}{2}\beta, 0)$ in the top diagram, and instead of the ordinate at B, the sum of 2 such areas from the top diagram. This leads to the expression

$$\frac{3}{4}\beta \left[\frac{e^r}{8} + \frac{32e^{\frac{3}{4}r}}{27} + \frac{r^3}{8} - \frac{19r^2}{48} - \frac{147}{216}r - \frac{283}{216} + \frac{1}{2} \left(1 - \frac{3}{2}\beta\right) \left\{ \frac{r^3}{3} + \frac{e^{r(1-\frac{3}{2}\beta)} - \frac{r^2(1-\frac{3}{2}\beta)^2 - r(1-\frac{3}{2}\beta) - 1}{(1-\frac{3}{2}\beta)^2} \right\} \right] \quad (48)$$

for an upper bound for the numerator.

Next, to get a lower bound for the denominator, one can obtain an ordinate smaller than that of B by taking the area under the lines 1 and 2 in the top diagram.

This area is

$$\int_0^{q_A} \left\{ \frac{r^4}{24}q + \frac{r^3}{3} \right\} dq + \int_{q_A}^1 \left\{ [(r-3)e^r + \frac{r^2}{2} + 2r + 3]q - (r-4)e^r - r^2 - 3r - 4 \right\} dq$$

where $q_A = \frac{(r-4)e^r + r^2 + 3r + 4 + \frac{r^3}{3}}{(r-3)e^r + \frac{r^2}{2} + 2r + 3 - \frac{r^4}{24}}$

Letting this area equal R, and using the area under the lines 3 and 4 in the diagram, one obtains as a lower bound for the denominator the expression

$$\int_0^{u_c} \frac{r^3}{3} u du + \int_{u_c}^1 \left\{ [e^r - \frac{r^2}{2} - r - 1]u + R - e^r + \frac{r^2}{2} + r + 1 \right\} du \quad (49)$$

where $u_c = \frac{e^r - \frac{r^2}{2} - r - 1 - R}{e^r - \frac{r^2}{2} - r - 1 - \frac{r^3}{3}}$

Evaluating (48) and (49) for $r_0 = 5$ and $r_0 = 10$ gives

as upper bounds for (47) the values 110 percent, 50 percent respectively. These values are not very impressive, but then the approximations made in obtaining bounds for the integrals in (47) were very crude. It would require a great deal of computation to make them more accurate, but at least, the way in which this can be done has been made clear by the above discussion.

2.3 The p State

Finally, consider the application of de Boer's method to a p state, for example the state with $n = 2$.

Here de Boer would take for the perturbed atom $a = 2 + \beta$ and $E \sim -1/4 + 1/4 \beta$, just as in the previous case. From (6), the recurrence relation this time is

$$\begin{aligned} b_s \{s(s-1) - 2\} &= b_{s-1} \left\{ 2 \frac{s-1}{2+\beta} - 2 \right\} \\ &= 2 b_{s-1} \frac{s-3-\beta}{2+\beta} \end{aligned} \quad (50)$$

which, neglecting β with respect to 2 leads to

$$b_2 = 1 \quad b_s = \frac{-\beta(s-3)!}{[s(s-1)-2][(s-1)(s-2)-2] \dots [3(2)-2]} \quad (51)$$

The corresponding wave function is

$$\Psi(r) = e^{-\frac{r}{2+\beta}} \left\{ r - \beta \sum_3^{\infty} b'_s r^{s-1} \right\} \quad (52)$$

$$\text{with } b_s = -\beta b'_s$$

The value of β is obtained as before, by demanding that this vanish for $r = r_0$.

$$\beta = \frac{r_0}{\sum_3^{\infty} b'_s r_0^{s-1}} \quad (53)$$

The values for $r_0 = 5$ and 10 are given.

r_0	β
5	.39
10	.041

As in the previous case, the value of β for $r_0 = 5$ is not small compared to 2 ; and therefore, de Boer's approximation is again relatively crude.

The exact $f(r)$ in this case is

$$r^2 + \sum_3^{\infty} \frac{2^{s-2} (s-3-\beta)(s-4-\beta) \dots (-\beta) r^s}{(2+\beta)^{s-2} \{s(s-1)-2\} \{(s-1)(s-2)-2\} \dots \{3(2)-2\}} \quad (54)$$

It is not as straightforward a matter this time to obtain good bounds for (54) as in the previous cases, but a set of bounds very similar to the ones found in (43) can be obtained by doing the following.

$$(54) \geq r^2 + \sum_3^{\infty} \frac{2^{s-2} (s-3)(s-4) \dots (-\beta) r^s}{2^{s-2} \{s(s-1)-2\} \{(s-1)(s-2)-2\} \dots \{3(2)-2\}} \quad (55)$$

The right hand side of (55) would be de Boer's $f(r)$. But (55) in turn is equal to

$$r^2 + \sum_3^{\infty} \frac{2 (s-3)! (-\beta) r^s}{s! (s-1)! \left\{1 - \frac{2}{s(s-1)}\right\} \left\{1 - \frac{2}{(s-1)(s-2)}\right\} \dots \left\{1 - \frac{2}{3 \cdot 2}\right\}}$$

$$\text{which is } \geq r^2 + \sum_3^{\infty} \frac{2 (-\beta) r^s}{s! (s-1)(s-2)}$$

$$= r^2 - \beta \sum_3^{\infty} \frac{2^{s-1} r^s}{s! (s-1)(s-2)} \quad (56)$$

$$\begin{aligned}
 \text{Also (54)} &\leq r^2 + \sum_3^{\infty} \frac{2^{s-2}}{(2+\beta)^{s-2}} \frac{(s-3-\beta)(s-4-\beta)\dots(-\beta)r^s}{s!(s-1)!} \\
 &= r^2 + \frac{(-\beta)r^3}{3!(2+\beta)} + \sum_4^{\infty} \frac{2^{s-2}(1-\frac{\beta}{s-3})(1-\frac{\beta}{s-4})\dots(-\beta)r^s}{(2+\beta)^{s-2}s!(s-1)(s-2)} \\
 &\leq r^2 + \sum_3^{\infty} \frac{2^{s-2}(1-\beta)^{s-2}(-\beta)r^s}{(2+\beta)^{s-2}s!(s-1)(s-2)} \\
 &= r^2 - \beta \sum_3^{\infty} \frac{r^s}{s!(s-1)(s-2)} \left\{ 2 \frac{1-\beta}{2+\beta} \right\}^{s-2} \\
 &\leq r^2 - \beta \sum_3^{\infty} \frac{r^s}{s!(s-1)(s-2)} \left\{ 2 \frac{1-\beta}{2+\beta} \right\}^{s-1} \tag{57}
 \end{aligned}$$

Combining (55), (56) and (57),

$$-\beta \sum_3^{\infty} \frac{2^{s-1} r^s}{s!(s-1)(s-2)} \leq \text{de Boer Series} \leq \text{Exact Series} \leq -\beta \sum_3^{\infty} \frac{r^s}{s!(s-1)(s-2)} \left\{ 2 \frac{1-\beta}{2+\beta} \right\}^{s-1} \tag{58}$$

and using $G(t)$ as defined before, this leads to

$$-\beta G(2) \leq \text{Exact Series} \leq -\beta G(1 - \frac{3}{2}\beta) \tag{59}$$

Rewriting

$$\begin{aligned}
 &-\beta \int_0^2 du \int_0^u \frac{e^{r_1 q} - \frac{r_1^2 q^2}{2} - r_1 q - 1}{q^3} dq \\
 &\leq \text{Exact Series} \\
 &\leq -\beta \int_0^{1-\frac{3}{2}\beta} du \int_0^u \frac{e^{r_1 q} - \frac{r_1^2 q^2}{2} - r_1 q - 1}{q^3} dq \tag{60}
 \end{aligned}$$

Thus the maximum percentage error that can arise will be

$$\frac{\int_{1-\frac{3}{2}\beta}^2 du \int_0^u \frac{e^{r_1 q} - \frac{r_1^2 q^2}{2} - r_1 q - 1}{q^3} dq}{\int_0^2 du \int_0^u \frac{e^{r_1 q} - \frac{r_1^2 q^2}{2} - r_1 q - 1}{q^3} dq} \times 100 \% \tag{61}$$

The numerator of (61) is at least half as large as the denominator, so not very good results will be obtained by using

this, and for this reason no values have been calculated.

The reason that this expression for the maximum percentage error is less satisfactory than those found previously, is that, in this case, the de Boer series does not lead immediately to an integral. In fact, it is of such an awkward form that a further approximation has to be made before a series expressible as an integral can be obtained. However, (56) is not the best possible next approximation to the de Boer series. Only computational hazards lie in the way of getting a better approximation to the maximum percentage error with which to replace (61).

CONCLUSION

In conclusion, it may be said that de Boer's method leads to reasonable values for the change in the eigenvalues for quite small r when the ground state is considered. But the above statement is not true for other states. For it was seen in the last two cases investigated that for $r = 5$, the value of β found did not justify using de Boer's method for a first approximation to the change in the energy. But when a larger value of r was taken (here, $r = 10$) a value of β was obtained that actually was small compared to 2. It may be inferred, from the discussion of the last two cases, that, in general, increasing either l or n will lead to increasing the lower bound to the range of values of r for which reasonable results are obtained.

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