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VARIABLE SCALING METHOD AND STARK EFFECT IN HYDROGEN ATOM *

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ABSTRACT

By relating the Stark effect problem in hydrogen-like atoms to that of the spherical anharmonic oscillator we have found simple formulas for energy eigenvalues for the Stark effect.

Matrix elements have been calculated using O(2,1) algebra technique after Armstrong and then the variable scaling method has been used to find optimal solutions. Our numerical results are compared with those of Hioe and Yoo and also with the results obtained by Lanczos.

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I. INTRODUCTION

Some time ago Hioe and Yoo (1980) derived perturbation series for weak and strong field for approximating resonances of the Stark effect.

It was pointed out long ago by Titchmarsh(1958) that a hydrogen atom in the presence of an electric field has no discrete energy eigenvalues. However, the perturbation series is useful if considered as an approximation to a pole of the perturbed Green's function. The poles are interpreted as resonances. The Borel summability of the perturbation series for the resonances of the Stark effect was shown by Graffi and Grecchi (1978) and by Herbst and Simon (1978).

Graffi et al. (1979) showed that the convergence of the diagonal Padé approximants sequence. The method employed by Hioe and Yoo is essentially that of finding the inverse of elliptic integral functions. This method is rather difficult and cumbersome and for strong field one needs many terms.

In this note we relate the problem of the Stark effect to that of spherical anharmonic oscillator and use the O(2,1) algebra technique after Armstrong (1971) for finding the matrix elements of r^s taken between the three-dimensional harmonic oscillator radial functions. We then use the variable scaling method to find the energy eigenvalues. This method gives simple algebraic equations involving the eigenvalues from which energy eigenvalues are numerically evaluated. Numerically our results agree with those of Hioe and Yoo for weak fields but differ from their results for strong fields, particularly in the case when $n > 1$. But our results are consistent with those of Lanczos.

II. MATHEMATICAL METHODS

The Stark problem can be reduced to that of quartic anharmonic oscillator by the standard method using parabolic coordinates as described in any textbook on quantum mechanics (For example see Fock (1978)). We reproduce here the essential steps. The Schrödinger equation for the hydrogen atom in in the presence of an electric field directed along the z axis is

$$\nabla^2\Psi + 2\left(E + \frac{1}{r} - \epsilon z\right)\Psi = 0 , \tag{1}$$

In writing (1) we have used atomic units. In this unit the electric field intensity is the field produced by a proton at a distance equal to the radius of the first Bohr orbit of hydrogen, viz

$$e/a^2 = 5.142 \times 10^9 \text{ volt/cm} . \tag{2}$$

Hence even in very strong field of 10^5 or 10^6 v/cm, G will still be small. Now to solve (1), parabolic coordinates can be used in the following way:

$$\xi = \rho + z, \qquad \eta = \rho - z , \tag{3}$$

where $s^2 = x^2 + y^2$, x,y,z being the Cartesian coordinates.

Then putting $\xi = u^2$, $\eta = v^2$ and assuming a solution of (1) in the form

$$\psi = u^{-1/2} v^{-1/2} e^{im\phi} \chi_1(u) \chi_2(v) \tag{4}$$

equation (1) reduces to two separate equations, viz

$$-\frac{d^2\chi_1}{du^2} + \left[-2Eu^2 + \epsilon u^4 + \frac{m^2 - 1/4}{u^2}\right] \chi_1 = \kappa \chi_1 \tag{5}$$

and

$$-\frac{d^2\chi_2}{dv^2} + \left[-2Ev^2 - \epsilon v^4 + \frac{m^2 - 1/4}{v^2}\right] \chi_2 = (\kappa' + 4) \chi_2 \tag{6}$$

with the condition

$$\kappa_{n_1,m} + \kappa'_{n_2,m} = 0 . \tag{7}$$

We consider equations (5) and (6) as perturbation problems and use variational analysis to tackle these equations. We describe the procedure for equation(5) and equation (6) can be treated in a similar manner. Using the change of variables

$$u_1 = \omega_0^2 u , \tag{8}$$

where $\omega_0^2 = \sqrt{-2E}$ (5) can be written as

$$-\frac{d^2\chi_1}{du_1} + \left[u_1^2 + g u_1^4 + \frac{(m^2 - 1/4)}{u_1^2}\right] \chi_1 = \kappa \chi_1 , \tag{9}$$

where

$$g = \frac{\epsilon}{\omega_0^6} . \tag{10}$$

To solve (9) we use as trial wave functions, spherical harmonic oscillator wave functions of a certain frequency ω and angular momentum ℓ given by $\ell = m - 1/2$.

Now equation (9) can be written as

$$H \chi_1 = \kappa \chi_1 \tag{11}$$

where

$$H = p^2 + u_1^2 + g u_1^4 + \frac{(m^2 - 1/4)}{u_1^2} . \tag{12}$$

The trial wave functions $\bar{\chi}$ say satisfies the Schrödinger equation given by the

$$H_0 \bar{\chi} = E_{n_1,\ell} \bar{\chi} , \tag{13}$$

where

$$H_0 = p^2 + \omega^2 u_1^2 + \frac{(m^2 - 1/4)}{u_1^2} \tag{14}$$

then $E_{n_1,\ell} = 2(2n_1 + m + 1)$

(15)

(the factor 2 appears in equation (5) because of our definition for H_0 (equation (14)). For a variational analysis of the energy κ, given in (11), we calculate $\int \bar{\chi}^* H \bar{\chi} \, d\tau$ and minimize this quantity, subject to the condition $\int \bar{\chi}^* \bar{\chi} \, d\tau = 1$, with respect to ω (Epstein (1974), Moshinsky (1969)). Some time ago Armstrong (1971) calculated the matrix elements of r^s taken between eigenstates of spherical anharmonic oscillator. Armstrong used the results of O(2,1) algebra to calculate these matrix elements. Using the same technique the matrix elements $\int \bar{\chi}^* H \bar{\chi}\, d\tau$, can be calculated easily.

The general result is given by

$$\int_0^\infty u^s \bar{\chi}^*_{n_1,m}(u)\bar{\chi}_{n_2,m}(u)\,du$$

$$= \omega^{-s/2}(-1)^{\frac{n_1-n_2}{2}}\,\Gamma(m+1+s/2)\times$$

$$\times\left(\frac{\Gamma[\frac{1}{2}(n_2+m-\frac{1}{2})+1]\,[\frac{1}{2}(n_1-m-\frac{1}{2})]!\,[\frac{1}{2}(n_2-m-\frac{1}{2})]!}{\Gamma[\frac{1}{2}(n_1+m-\frac{1}{2})+1]}\right)^{1/2}\times$$

$$\times\sum_t \frac{(-1)^t}{[\frac{1}{2}(n_1-m-\frac{1}{2})-t]!\,[\frac{1}{2}(2m+n_2-n_1)+t+1]}\begin{pmatrix} s/2 \\ \frac{n_2-n_1}{2}+t\end{pmatrix}\times$$

$$\times\begin{pmatrix}\frac{n_1-n_2-s-2}{2} \\ t\end{pmatrix}, \qquad (17)$$

where the selection rules are such that when $|n_2-n_1|$ and s are both odd integers and if $s+2>0$, $n_2-n_1>s+2>0$

or $\quad n_1-n_2 \geq s+2>0$

or if $\quad s+2\leq 0,\ |n_1-n_2|\leq -s-2<0$

then the integral must be set equal to zero. Using (17) we get, taking $\kappa_{n_1,m}$ as the value of the diagonal elements of H,

$$K_{n_1,m} = \omega(2n_1+m+1) + \frac{(2n_1+m+1)}{\omega} +$$

$$+\frac{g}{\omega^2}\,[(m+2)(m+1)+6n_1(m+2)+3n_1(2n_1-1)] \qquad (18)$$

ω is determined by the condition that $\kappa_{n_1,m}$ should be minimum, viz,

$$\frac{\partial K_{n_1,m}}{\partial\omega} = 0 \qquad (19)$$

(19) with (18) give

$$\omega^3-\omega = \frac{2g\,[(m+2)(m+1)+6n_1(m+2)+3n_1(2n_1-1)]}{(2n_1+m+1)}. \qquad (20)$$

A similar analysis can be done for equation (6). Here we just give the results.

$$K'_{n_1,m} + 4/\omega_2^2 = \omega'(2n_2+m+1) + \frac{(2n_2+m+1)}{\omega'}$$

$$-\frac{g}{\omega'^2}\,\frac{[(m+2)(m+1)+6n_2(m+2)+3n_2(2n_2-1)]}{(2n_2+m+1)}, \qquad (21)$$

where ω^1 satisfies the equation

$$\omega'^3-\omega' = \frac{-2g'\,[(m+2)(m+1)+6n_2(m+2)+3n_2(2n_2-1)]}{(2n_2+m+1)}. \qquad (22)$$

Equations (18) to (22), together with the condition $\kappa_{n_1,m} + \kappa'_{n_2,m} = 0$, give three simultaneous equations for ω, ω' and ω_0^2. Solving them we get ω_0^2 and hence $\in$. For small $\in$, these equations can be solved by the following procedure. For the sake of simplicity, let us consider the case, $n_1 = n_2 = 0$. Then (18) to (22) reduce to

$$\omega^3 - \omega - 4g = 0 \tag{23}$$

$$\omega'^3 - \omega' + 4g = 0 \tag{24}$$

and

$$\omega + 1/\omega + \omega' + 1/\omega' + 2g\left(1/\omega^2 - 1/\omega'^2\right) - 4/\omega_0^2 = 0 \tag{25}$$

Assume, $\omega = 1 + \in$, $\omega' = 1 - \in$, $\omega_0^2 = x$ then it can be easily seen that x satisfies the equation

$$x^6 - x^5 + 2\epsilon^2 = 0 \tag{26}$$

Equation (26) can be solved numerically for x using Newton-Raphson's method, for a given $\in$.

III. SECOND ORDER CORRECTION

The second order correction to $\kappa_{n_1,m}$ and $\kappa'_{n_2,m}$ denoted by

$$K^{(2)}_{n_1,m} = \frac{\sum_p \langle n_1 | -(1+\omega^2) u_1^2 + g u_1^4 | p \rangle^2}{K^0_{n_1,m} - K^0_{n_1+p,m}} \tag{27}$$

and

$$K'^{(2)}_{n_2,m} = \frac{\sum_p \langle n_2 | -(1+\omega^2) v_1^2 - g v_1^4 | p \rangle^2}{K'^0_{n_2,m} - K'^0_{n_2+p,m}} \tag{28}$$

where $\kappa^0_{n_1,m}$ and $\kappa^0_{n_2,m}$ are given by equations (18) and (21), can easily be calculated using the technique of O(2,1) algebra (Armstrong (1971)). For the particular case, $n_1 = n_2 = 0$, $m = 0$, the energy equation up to second order is given by

$$\omega + 1/\omega + \omega' + 1/\omega' + 2g\left(1/\omega^2 - 1/\omega'^2\right) + \frac{4g^2}{\omega^4\left(\frac{K_{0,0}}{\omega_0^2} - \frac{K_{4,0}}{\omega_0^2}\right)} + \frac{4g^2}{\omega^4\left(\frac{K'_{0,0}}{\omega_0^2} - \frac{K'_{4,0}}{\omega_0^2}\right)} - 4/\omega_0^2 = 0 \tag{29}$$

IV. RESULTS AND DISCUSSIONS

Instead of giving the values of E directly we compute the quantity $-2(E-E_0)/\epsilon^2$, for the case $n_1 = n_2 = 0$, and $(E-E_0)/\epsilon$ otherwise.

In Table 1 we compare our values of $-2(E-E_0)/\epsilon^2$ with those obtained by Hioe and Yoo for $n_1 = n_2 = m = 0$. It is seen that for $\epsilon > 16 \times 10^{-3}$ our results differ from those of Hioe et al. It seems that the fourth-order corrections are not negligible for such values of electric field intensity. To see the fourth order effect, we assume

$$-2(E-E_0)/\epsilon^2 = 4.25 + s\epsilon^2 \tag{30}$$

and compute s from the approximate formula given by Lanczos (1931). Though Lanczos' results are very accurate only for $n > 1$, we use this formula to guess the order of magnitude of the fourth order corrections. We give the numerical results obtained from formula (30). Considering the fact that for $n_1 = n_2 = 0$, Lanczos' result would underestimate s, our results are not inconsistent with his results. In Table 2 we compare the values of $(E-E_0)/\epsilon$. Column (2) gives the results of Hioe et al. Column (3) gives those obtained from 3rd order formulas (Bethe and Salpeter (1957)). Column (4) gives the results of the present work. Lastly, column (5) gives the results computed from Lanczos' fourth order formula (Lanczos (1931), equation (66)).

It seems that for $n_1 = 10$, $n_2 = 0$, fourth order effect is significant even for moderate field strength of the order of 10^4 v/cm.

Thus our results agree with those of Hioe et al. for weak fields and where fourth order effects are significant our results are consistent with those of Lanczos.

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TABLE 1

$$\Delta = -2(E - E_0)/\epsilon$$

ϵ	Δ(Hioe et al.)	Δ(present)	Δ(Lanczos)
.016	4.25	4.25	4.25
.032	4.25	4.27	4.26
.048	4.25	4.29	4.27
.06	–	4.44	4.29

TABLE 2

$$\Delta_1 = (E - E_0)/\epsilon$$

ϵ	Δ_1(H)	Δ_1 (BZS)	Δ_1(P)	Δ_1(L)
6.4×10^{-6}	156.3	156.6	159.4	156.6
8×10^{-6}	154.3	155.2	157.0	155.0
16×10^{-6}	145.9	151.7	145.8	150.0