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Semi-classical and Envelope Methods in Quantum Mechanics

J. Paul Duarte

A Thesis

in

The Department

of

Physics

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science at
Concordia University
Montréal, Québec, Canada

February 1992

ISBN 0-315-73675-5

ABSTRACT

Semi-classical and Envelope Methods in Quantum Mechanics

J. Paul Duarte

The nature and quality of Schrödinger-eigenvalue approximations obtained by the *JWKB* method are explored. The relation between *JWKB* and the method of potential envelopes is studied. The interesting connection between the large-N approximation and the potential envelope method is reviewed. Both the *JWKB* approximation and the method of potential envelopes are employed to explore the bound state spectrum of a single particle in the potential $V(r) = \frac{\beta}{r} + \frac{\gamma}{r}e^{-\lambda r}$, $\gamma < \beta$. These approximate energies are compared with eigenvalues computed numerically by a finite-element method, and also with the results of an independent variational calculation.

ACKNOWLEDGEMENTS

I would like to take this opportunity to offer heart-felt thanks to my advisor, Dr. R.L. Hall, for suggesting the topic, for his unwavering support and guidance and also for the financial assistance during the preparation of the thesis.

The assistance provided by X. Li is greatly appreciated.

The financial support of the Concordia University Physics Department made being a student a less stressful experience.

My deepest gratitude goes to my mom M. Duarte, my dad J. Duarte and my grandmother M.C. Duarte without whose love and support over the years this work would not have been possible.

For the tireless support and for correcting many a grammatical error during the preparation of this thesis I am deeply indebted to N. Allard. Thanks for always being there when it mattered and for putting up with me!

The smooth operation of computer software and hardware often calls for expert intervention; D. Chu led many a successful technical rescue mission and his help is much appreciated since it was essential to the completion of the this work.

A special thanks to G. Thomson and L. Chapman of the

Concordia University Physics Department for all their assistance.

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INTRODUCTION

The physics of the last few centuries has been dominated by the mathematical construct known as the differential equation. In every field of modern physics one encounters equations which often can best be expressed in the language of the differential calculus. However, just as equations in differential form are ubiquitous, exact solutions of such equations are rare.

Of particular interest are differential equations of the second order with variable coefficients, of the form

$$\frac{d^2\psi}{dx^2} + p(x)\frac{d\psi}{dx} + q(x)\psi = 0.$$

Such equations possess exact solutions only if p and q are selected from a very small number of standard cases. A special case of this general form occurs in nonrelativistic quantum mechanics, and is known as the Schrodinger equation. The time-independent version is given by

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = \mathcal{E}\psi(x).$$

This eigenvalue equation describes the spatial configuration of a stationary state. Yet, the Schrodinger

equation can only be solved exactly for a small number of potentials V. Of course, with the advent of the digital computer numerical solutions can always be obtained. However, it is sometimes desirable to have at our disposal analytical methods of approximating the solutions. often, only the energy levels $\mathcal{E}$ of the state of the system in question are required and many approximation techniques have been developed to handle just this problem. Two such approaches are: the method of potential envelopes and the *JWKB* approximation. The method of potential envelopes provides bounds to the eigenvalues for a given potential. In 1986 R.L. Hall[1] showed that these bounds can be employed to deduce that the large-N approximation also provides bounds to the eigenvalues which happen not to be as tight as those of envelope theory. An interesting question then arises, can a similar connection be found between the potential envelope method and other semi-classical approximation techniques? In this thesis we seek to answer this question as it applies to the *JWKB* approximation.

In chapter 1 we examine the theory behind the method of potential envelopes. To motivate the discussion on the *JWKB* method in chapter 3 we present a synopsis of the results of Hall's work on the large-N approximation. Chapter 3 is devoted to an in-depth analysis of the *JWKB* approximation

and its possible connection to the potential envelope method. Finally, in chapter 4, the potential envelope method and the *JWKB* approximation are employed to compute the approximate bound-state energies of the Coulomb-plus-Yukawa potential. This potential was the subject of a paper by the present author and R.L. Hall entitled: "Spectrum of the Coulomb-plus-Yukawa potential by the Method of Potential Envelopes" (see appendix B). It is found that although potential envelopes provide good approximations to the energies, the results of the *JWKB* method are even closer to the true energies, thus precluding any possibility of a comparison of the type outlined in chapter 2. Future research into potential envelope theory, aimed at strengthening the energy bounds, may alter this present state of affairs.

CHAPTER 1
THE METHOD OF POTENTIAL ENVELOPES

Exact solutions of differential equations are in general hard to come by. Thus, methods of approximating such solutions are always of particular interest. Over the last few decades much effort has been made to find approximate solutions of the Schrödinger equation. Many different schemes have been proposed. Recently, Hall[2,3] has developed one such technique for approximating the bound-state spectrum of Schrödinger Hamiltonians. This new approach, known as the *method of potential envelopes*, has advantages over other methods; for a wide class of problems it provides a simple formula for *bounds* to the eigenvalues. A more general formulation of this geometrical theory, described in ref. (3), allows also for *sums* of soluble potential terms. The method of potential envelopes was developed in 1980 as a means of approximating the eigenvalues of the many body problem[4]. Since then it has been refined[2,3,5] and applied to a variety of problems[1,6-9].

The main purpose of this thesis is to compare the relative quality of the results of the method of potential envelopes and the *JWKB* approximation. We begin this study with a discussion of envelope theory.

1.1 The theory of potential envelopes

For spherically symmetric problems in $\mathbb{R}^3$ the Schrödinger equation takes the following form

$$\left[-\frac{\hbar^2}{2m}\Delta + V(r)\right]\psi(r) = \mathcal{E}\psi(r), \tag{1.1}$$

where $\mathcal{E}$ is the energy and the central potential $V(r)$ ($r = |\vec{r}|$) can be expressed as

$$V(r) = V_0 f(r/a), \quad V_0 > 0, \; a > 0. \tag{1.2}$$

This way of representing V explicitly disentangles the contributions made by the strength, V_0, and the shape, $f(r/a)$, of the potential. In order to simplify our notation we make the following change of variables; $r/a \longrightarrow r$.
Thus, (1.1) becomes

$$[-\Delta + \upsilon f(r)]\psi(r) = E\psi(r), \quad \upsilon > 0, \tag{1.3}$$

with E and ω respectively defined to be

$$E = 2m\mathcal{E}a^2/\hbar^2,$$
$$\omega = 2mV_0a^2/\hbar^2. \tag{1.4}$$

Therefore, we see from (1.3) that for spherically symmetric problems in nonrelativistic quantum mechanics the Hamiltonian can be expressed in the form

$$H = -\Delta + \omega f(r), \quad \omega > 0, \tag{1.5}$$

where f is a central potential and ω a coupling constant. In particular we will consider potentials which satisfy the following conditions

$$\begin{aligned} &(i) \quad \lim_{r\to 0} |r^2 f(r)| = 0, \\ &(ii) \quad f'(r) > 0, \quad r > 0. \end{aligned} \tag{1.6}$$

Restricting f in this manner means that H is self-adjoint on some domain $\mathcal{D}(H) \subset L^2(\mathbb{R}^3)$, and also that, for ω sufficiently large, discrete eigenvalues are guaranteed to exist. We assume that ω is such that discrete eigenvalues $E_{n\ell}$ exist, where $\ell = 0,1,2,\ldots$, is the angular-momentum quantum number and $n = 1,2,3,\ldots$, counts the eigenvalues in each angular-momentum subspace. These eigenenergies are ordered according to $E_{n'\ell} \geq E_{n\ell}$, $n' > n$, which implies that for a

given ℓ and n, $E_{n\ell}$ has degeneracy exactly $2\ell + 1$. The curves describing the dependence of the $E_{n\ell}$ on ω we call the *energy trajectories* of f, which can be written as

$$E_{n\ell} = F_{n\ell}(\omega). \tag{1.7}$$

The method of potential envelopes is a technique for approximating the energy trajectories of Schrödinger Hamiltonians which are not exactly soluble.

Having defined the nature of the problem at hand we now turn our attention to the particulars of envelope theory. The foundations of the potential envelope method rely on two central concepts: envelope representations and the variational characterization of eigenvalues. We will deal with each of these in turn beginning with the method of functional representation known as the envelope representation.

1.2 Envelope representations

Many varieties of functional representation exist. One such technique relies on the fact that smooth functions possess a unique tangent at every point. The family consisting of all lines tangent to the curve defines the function completely.

Consider an arbitrary smooth function $V(r)$ defined on a given interval. Any line tangent to V can be succinctly expressed as

$$V^{(t)}(r) = A + Br, \tag{1.8}$$

where t refers to the point of contact between the tangent line and the curve $V(r)$ and A,B are constants which depend on t (see fig.1.1). It is also clear that the following relations hold

$$\begin{aligned} V(t) &= A + Bt, \\ V'(t) &= B, \end{aligned} \tag{1.9}$$

which allows us to eliminate A and B in (1.8) as follows

$$V^{(t)}(r) = V(t) - tV'(t) + V'(t)r. \tag{1.10}$$

We call $V(r)$ the envelope (curve) of the collection of these tangent lines, namely

$$V(r) = \underset{t}{Envelope}\ V^{(t)}(r). \tag{1.11}$$

For our purposes, it is necessary to generalize the condition (1.8). That is, we must consider the case where the curves tangent to $V(r)$ are not straight lines. Thus, we are interested in examining how (1.10) is transformed if the

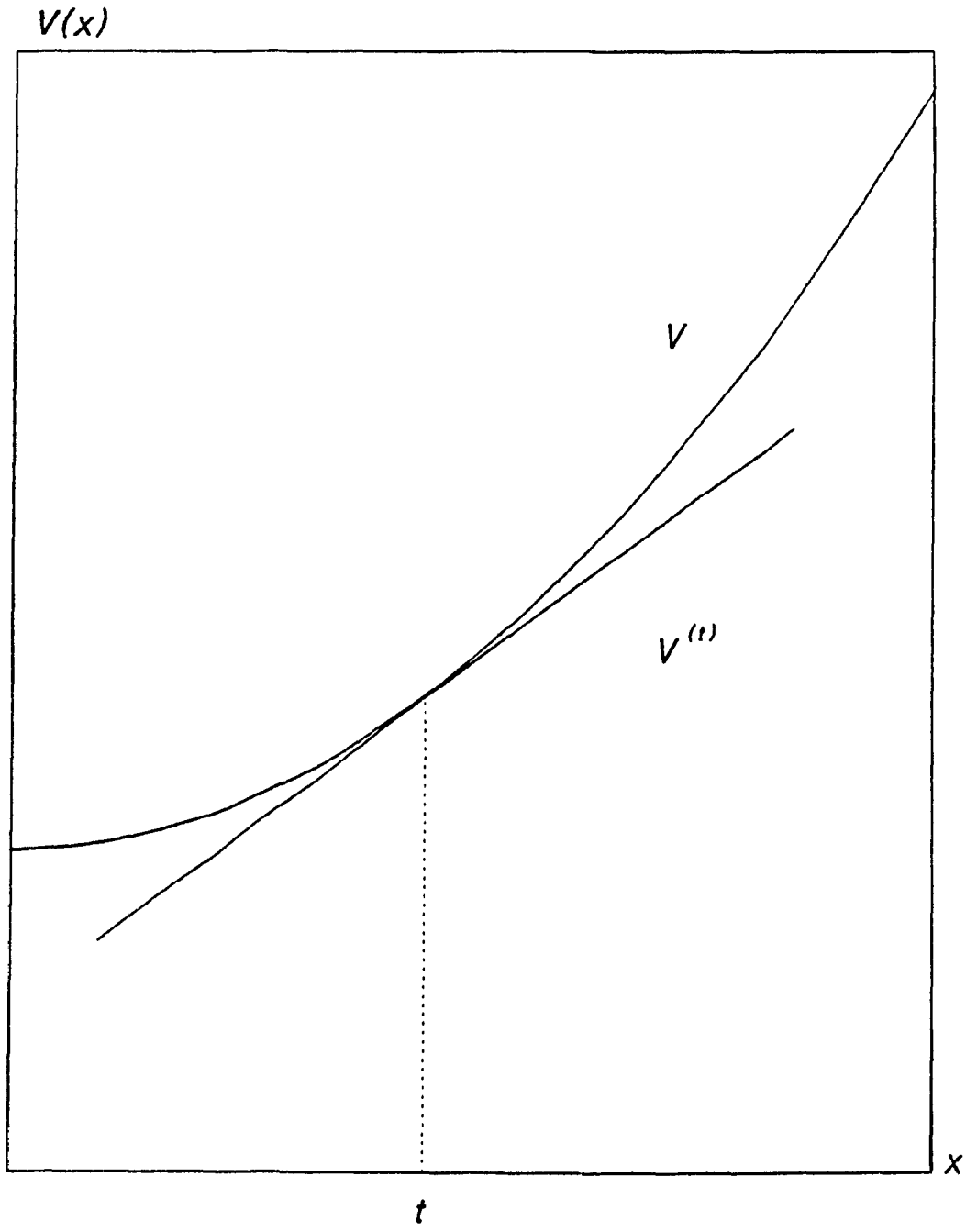

Fig.1.1 Tangent basis potentials, $V^{(t)}$, to the potential V.

following change of variables is made:

$$V(r) = g(h(r)), \tag{1.12}$$

where $h(r)$ is now the curve tangent to V and g is a smooth increasing transformation. In a manner analogous to that outlined above, g considered as a function of h, can be expressed as the envelope of its tangents. Thus, we have

$$g(h) = \underset{T}{Envelope}\ g^{(T)}(h), \tag{1.13}$$

where

$$g^{(T)}(h) = g(T) - Tg'(T) + g'(T)h. \tag{1.14}$$

If we select the variable T itself to be the tangent curve, as follows

$$T = h(t), \tag{1.15}$$

then the tangents to g can be written in an alternate manner, namely

$$g^{(t)}(h(r)) = g(h(t)) - h(t)g'(h(t)) + g'(h(t))h(r), \tag{1.16}$$

which can be expressed more simply as

$$g^{(t)}(h(r)) = A(t) + v(t)h(r), \tag{1.17}$$

with

$$A(t) = g(h(t)) - h(t)g'(h(t)), \; v(t) = g'(h(t)), \; t \in (0,\infty), \tag{1.18}$$

where we have restricted the domain of t such that (1.18) is applicable to the theory set out below. As a result of the above manipulations, the function $V(r)$ can then be expressed as

$$V(r) = g(h(r)) = \underset{t}{Envelope}\; g^{(t)}(h(r)). \tag{1.19}$$

where $h(r)$ is any curve which is tangent to $V(r)$ at a single point.

We are of course interested in applying this theory to the problem of approximating Schrödinger eigenvalues. The reason for considering envelope representations in this regard is that we wish to represent potentials for which the Schrödinger equation is intractable by those for which it has exact solutions — the backbone of potential envelope theory is this exploitation of exact solutions. Thus, we consider the function $h(r)$ to be a potential for which the energy trajectories $G_{n\ell}(v)$ of the Schrodinger Hamiltonian

$-\Delta + \omega h(r)$ are exactly known. The Hamiltonian whose energy trajectories $F_{n\ell}(\omega)$ we are interested in approximating will be given by $-\Delta + V(r)$. Here, the potential $V = g(h(r))$ is equivalent to the function V defined above and, naturally, subject to the same constraints (eqn. (1.6)). In addition, we assume that g is either *convex* or *concave*, that is to say either $g'' > 0$ or $g'' < 0$. We will show below that these cases give rise to lower or upper energy bounds respectively.

1.3 The variational characterization of eigenvalues

Any eigenvalue of H can be expressed as the solution to a certain variational problem. The following theorem states this result succinctly:

Min-Max (Rayleigh-Ritz) Theorem:

For a given angular-momentum subspace labelled by ℓ the eigenvalue $E_{n\ell}$ of the self-adjoint operator H is equal to

$$E_{n\ell} = \inf_{\mathcal{D}_n} \sup_{\substack{\psi \in \mathcal{D}_n \\ \|\psi\| = 1}} (\psi, H\psi), \tag{1.20}$$

where $\mathcal{D}_n \subset \mathcal{D}$ is a finite-dimensional subspace of fixed dimension n given by $\mathcal{D}_n = \mathrm{Span}\{\psi_1, \psi_2, \ldots, \psi_n\}$.

A proof of this theorem is beyond the scope of this thesis but can be found in a number of texts which deal with the functional analysis of nonrelativistic quantum mechanics[10-12]. The text by Epstein contains an interesting discussion of the finite dimensional case[13]. What the min-max theorem tells us is that by restricting the domain of H in a particular way ($\mathcal{D}_n$) we ensure that the result of maximizing the Rayleigh-quotient is an upper-bound to the eigenvalue $E_{n\ell}$. In fact, each $\mathcal{E}_k = sup(\psi,H\psi)$ is an upper bound to the corresponding eigenvalue $E_{k\ell}$, $k = 1,2,3,\ldots,n$ (fig.1.2) (An interesting analogy is the general increase in vibrational frequencies that occurs when more stringent constraints are imposed on an oscillating membrane[14]). By searching all subspaces $\mathcal{D}_n$ of fixed dimension n we find that the minimum of all the maxima is the exact eigenvalue $E_{n\ell}$.

1.4 Wedding min-max to envelope representations

What makes the min-max theorem so valuable in the present context is that it allows us to place bounds on the eigenvalues $E_{n\ell}$ of the Hamiltonian given bounds on the potential $V(r)$. To bound the potential all that is required is for the convexity of the function g (defined above) to be definite. To make the present discussion more concrete we

The Min-Max Theorem

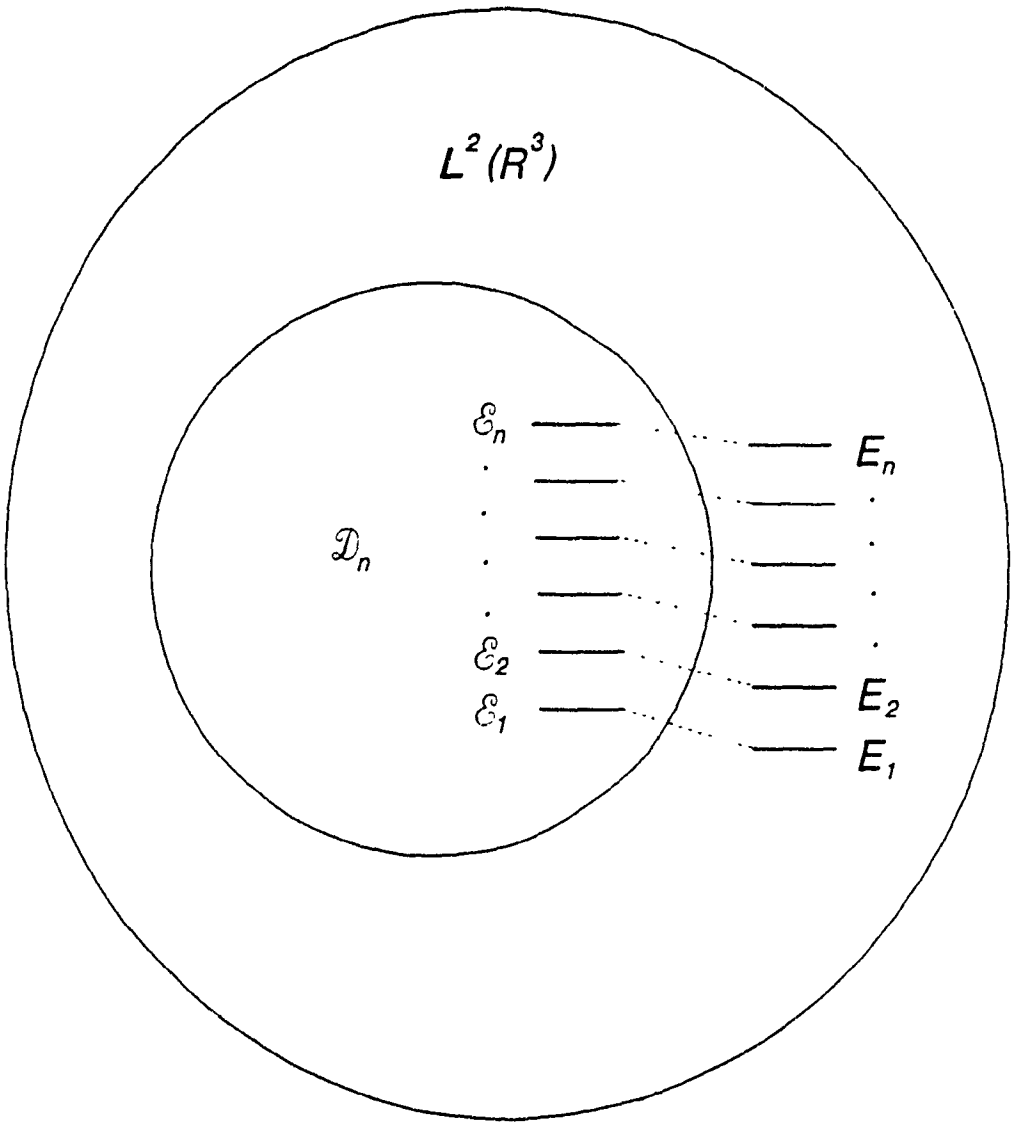

Fig.1.2 Illustration of the min-max theorem.

will assume that g is concave so that $g'' < 0$. This condition ensures that the tangent lines to g (as a function of h) all lie above g. Thus, the relationship between the potential $V(r)$ and the basis potential $h(r)$ becomes

$$V(r) = g(h(r)) \leq A(t) + \omega(t)h(r), \tag{1.21}$$

where $A(t)$ and $\omega(t)$ are defined as in (1.18) and $h(t)$ is the point where $V(r)$ and its tangent potential $V^{(t)}(r)$, given by the right-hand side of (1.21), coincide. By substituting the Hamiltonian $H = -\Delta + V(r)$ into the expression (1.20) provided by the min-max theorem, we immediately obtain an *upper bound* to the eigenvalues of H, namely

$$E_{n\ell} \leq A(t) + G_{n\ell}(\omega(t)), \tag{1.22}$$

which is equivalent to

$$E_{n\ell} \leq g(h) - hg'(h) + G_{n\ell}(g'(h)). \tag{1.23}$$

To find the best upper bound to $E_{n\ell}$ we minimize (1.23), considering it a function of h. The critical point is simply

$$h = G'_{n\ell}(g'(h)). \tag{1.24}$$

A very convenient way of writing this optimum upper bound can be achieved by applying a Legendre transformation. Reordering the terms in (1.23) we can write

$$E_{n\ell} \leq G_{n\ell}(g'(h)) - g'(h)h + g(h). \tag{1.25}$$

We then define the best upper bound to be

$$E_{n\ell} \leq \min_{r>0} \left\{ K_{n\ell}(r) + V(r) \right\}, \tag{1.26}$$

where

$$K_{n\ell}(r) = G_{n\ell}(s) - sG'_{n\ell}(s), \quad h(r) = G'_{n\ell}(s). \tag{1.27}$$

It has been shown by Hall[2] that $G_{n\ell}$ is concave. As a result, the functions $K_{n\ell}(r)$ are well defined by (1.27). This implies that $G'_{n\ell}$ is monotone and is invertible. The variable t has been replaced by r since due to the presence of $V(r)$, it seems a more natural way of expressing the energy bounds. Thus, we have shown that bounds can be imposed on the energies $E_{n\ell}$ if the potential $V(r)$ can be expressed as a transformation $g(h(r))$ of the potential $h(r)$ whose convexity is definite. When the transformation $g(h(r))$ is concave we obtain an upper bound and when it is convex the inequalities are reversed and (1.26) becomes a lower bound. It should be noted that the formula (1.26) also applies in the one-dimensional case, where of course

the energies depend only on n, that is, $E_{n\ell} \longrightarrow E_n$.

To prepare the groundwork for later chapters we consider two special cases: (a) potentials which can be expressed as smooth transformations of the Coulomb potential $h(r) = -1/r$, and (b) those potentials which are representable as transformations of the simple harmonic oscillator potential in one-dimension, $h(x) = x^2$.

(a) The energy trajectories for this particular basis potential are given by

$$G_{n\ell}(v) = -\left[\frac{v}{2(n + \ell)} \right]^2, \tag{1.28}$$

which, through (1.27), results in $K_{n\ell}(r) = [(n + \ell)/r]^2$. Thus, the expression for the energy (eqn. (1.26)) becomes:

$$E_{n\ell} \approx \min_{r>0} \left\{ \frac{(n + \ell)^2}{r^2} + V(r) \right\}, \quad n = 1,2,3,\ldots, \tag{1.29}$$

where $V(r) = g(-1/r)$; and $\approx = \leq$ if g is concave, and $\approx = \geq$ if g is convex. If the transformation function g is slowly varying, then, as we shall see, this simple formula is remarkably useful for it answers the question, how does the spectrum depend on the potential? It is also interesting that the transformation function does not appear in (1.29); g is only used to establish the energy bound.

(b) In this case the energy trajectories for $h(r)$ are

$$G_n(\omega) = (2n - 1)\sqrt{\omega}, \tag{1.30}$$

which implies that the $K_n(x) = [(n - 1/2)/x]^2$. The energies associated with $V(x)$ are then approximated by

$$E_n \approx \min_{x>0} \left\{ \frac{(n - 1/2)^2}{x^2} + V(x) \right\}, \quad n = 1,2,3,\ldots, \tag{1.31}$$

where $V(x) = g(x^2)$; and $\approx = \leq$ if g is concave, and $\approx = \geq$ if g is convex.

A specific application of the method of potential envelopes is presented in chapter 4. We next explore how the method of potential envelopes is related to the large-N approximation.

CHAPTER 2
POTENTIAL ENVELOPES AND THE LARGE-N APPROXIMATION

One of the most original approximation schemes for Schrödinger eigenvalues to have been developed in the last few years is the large-N approximation. By manipulating the Schrödinger equation in N *spatial dimensions* it is possible to derive a relation which allows one to approximate the eigenvalues of a given Hamiltonian in $\mathbb{R}^3$. The technique is perturbative in nature employing $1/N$ (or more precisely $1/(N + 2\ell)$) as the expansion parameter. In contrast to perturbation theory however, this $1/N$ expansion is not restricted to problems where the Hamiltonian is expressed as the sum of two terms — one solvable and the other small in some suitably defined sense. Our main intention in this chapter is to relate how large-N and the method of potential envelopes are connected. This was the subject of a 1986 paper by Hall[1] in which the theory set out below was developed. As stated in the introduction, this chapter is intended to act as a bridge, motivating the attempt at establishing a relationship between potential envelopes and *JWKB* later on in chapter three.

Large-N theory was first developed in the area of critical phenomena[15]. Over the years it has seen many applications in other fields, quantum field theory and solid-state for example[16,17]. More recently it has been employed to solve the Schrödinger equation[18].

2.1 Large-N theory

In this last branch of the theory, the Schrodinger equation

$$\left[-\tfrac{1}{2}\Delta + V(r)\right]\psi = E\psi \tag{2.1}$$

is written down in N spatial dimensions, the radial part of which is given by

$$\left\{-\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{N-1}{r}\frac{d}{dr}\right] + \frac{\ell(\ell+N-2)}{2r^2} + V(r)\right\}\psi(r) = E\psi(r), \tag{2.2}$$

where the factor of $\frac{1}{2}$ in front of the Laplacian in (2.1) is in place so that the results of envelope theory can be compared with those of large-N theory, which employs this convention. If we rewrite the wave function as

$\psi(r) = r^{-(N-1)/2}R(r)$ then (2.2) can be expressed in the form

$$-\frac{1}{2}\frac{d^2}{dr^2}R(r) + \left[\frac{1}{2}\beta r^{-2} + V(r)\right]R(r) = ER(r) \tag{2.3}$$

with

$$\beta = \left[\ell + \frac{1}{2}(N-1)\right]\left[\ell + \frac{1}{2}(N-3)\right]. \tag{2.4}$$

In the limit of large N the ground state energy for each angular-momentum subspace can be approximated by the minimum of the effective potential

$$V_{eff}(r) = \frac{1}{2}\beta r^{-2} + V(r). \tag{2.5}$$

This is the result of V_{eff} dominating in magnitude the differential term $-\frac{1}{2}R''(r)$. Thus we can write

$$E_{0\ell} \simeq E(\beta) = \min_{r>0}\left[\frac{1}{2}\beta r^{-2} + V(r)\right]. \tag{2.6}$$

Higher-order corrections to the ground-state energy can be obtained by making the following transformations

$$r \longrightarrow r_o(1+x),$$
$$V(r) \longrightarrow V\left(9r/N^2\right),$$
$$R(r) \longrightarrow exp\left[\phi(x)\right],$$

where r_o is the minimum of the effective potential $V_{eff}(r)$ and the last substitution transforms (2.3) into a Riccati

equation. Analytical techniques are then brought to bear to find the coefficients of the resulting energy expansion. Since our intention is to elucidate the connection between large-N and potential envelopes however, we will restrict our attention to the zeroth-order result, eqn.(2.6).

A recent significant improvement to the large-N approximation is known as the shifted large-N approximation[19]. Here the expansion parameter 1/k, where $k = N + 2\ell$, is replaced by $1/\bar{k}$ with $\bar{k} = k - a = N + 2\ell - a$, a being an appropriate shift. A much wider class of problems is amenable to this new approach. Also the accuracy of the results is higher than those produced with the large-N approximation[19].

There exist a few potentials for which the eigenvalues are exactly known for any number of dimensions N[1]. Two of the most important are the hydrogenic atom

$$V(r) = -\omega/r \longrightarrow \mathcal{E}_{n\ell}(\omega) = -\tfrac{1}{2}\omega^2\left[\ell + n + \tfrac{1}{2}(N-1)\right]^{-2}, \quad N \geq 2 \tag{2.7}$$

and the harmonic oscillator potential

$$V(r) = \omega r^2 \longrightarrow \mathcal{E}_{n\ell}(\omega) = (2\omega)^{1/2}\left[\ell + 2n + \tfrac{1}{2}N\right], \tag{2.8}$$

where $n = 0,1,2,\ldots$, is the radial quantum number and

$\ell = 0,1,2,\ldots$, is the angular-momentum quantum number. The square of the total angular-momentum is $L^2 = \ell(\ell + N - 2)$.

2.2 The connection between potential envelopes and large-N

In chapter 1 it was demonstrated that the eigenvalues of the Schrödinger Hamiltonian

$$-\tfrac{1}{2}\Delta + V(r) \tag{2.9}$$

can be approximated by the formula

$$E = \min_{r>0}\left[K(r) + V(r)\right] \tag{2.10}$$

where $V(r) = g(h(r))$, with $g(h)$ monotone increasing and $h(r)$ a potential for which the Schrödinger equation resulting from the Hamiltonian $-\tfrac{1}{2}\Delta + \omega h(r)$ can be solved exactly. And also

$$K(r) = \mathcal{E}(\omega) - \omega\mathcal{E}'(\omega) \quad \text{and} \quad h(r) = \mathcal{E}'(\omega) \tag{2.11}$$

with $\mathcal{E}(\omega)$ being the energy trajectory of the soluble

potential $h(r)$. For power-law potentials of the form

$$h(r) = sgn(q)r^q, \quad q \geq -1, \quad q \neq 0, \tag{2.12}$$

the energy trajectories are given by

$$\mathcal{E}(v) = sgn(q)Qv^{2/(2+q)}, \quad Q > 0, \tag{2.13}$$

which by (2.11) implies that $K(r)$ can be written as

$$K(r) = \tfrac{1}{2}\alpha r^{-2}, \quad \alpha = |q|\left[2Q/(2+q)\right]^{(2+q)/2}. \tag{2.14}$$

Therefore (2.10) now becomes

$$E = \min_{r>0}\left[\tfrac{1}{2}\alpha r^{-2} + V(r)\right], \quad \alpha > 0. \tag{2.15}$$

The formula (2.10) is now of the form (2.6) which is the main result of large-N theory. This allows a direct comparison to be made between the energy results of the two theories. Such comparisons revolve around the nature of the parameters α and β. An important result that must be considered in this respect is how the approximate energies

are ordered in relation to α. From (2.15) it is easy to see that

$$\frac{dE}{d\alpha} = \frac{1}{2}r^{-2} > 0 \tag{2.16}$$

which in effect states that $\alpha_1 > \alpha_2 \Rightarrow E(\alpha_1) > E(\alpha_2)$. This procedure for reformulating the eigenvalue formula (2.10) from potential envelopes was devised by Hall[1].

As an example of a comparison between the two theories in question, consider the class of potentials which can be expressed as *convex* transformations of the hydrogenic atom potential (2.7), that is, $V(r) = g(-1/r)$. An expression for the corresponding α can be deduced by comparing (2.7) with (2.14), that is

$$\alpha_1 = \left[\ell + n + \tfrac{1}{2}N - \tfrac{1}{2}\right]^2. \tag{2.17}$$

Inspecting (2.4) and (2.17) for the case $n = 0$ we can deduce that the parameters α, β are ordered as $\beta < \alpha_1$ which due to the ordering of the energies with α, (2.16), immediately implies the inequalities

$$E(\beta) < E(\alpha_1) \leq E_{0\ell}. \tag{2.18}$$

Therefore, we see that the large-N approximation results in a *lower-bound* to the true energy and that this bound is

weaker than that provided by potential envelopes. A similar analysis can be applied to those potentials which can be written as convex transformations of the harmonic oscillator potential (2.8). In this case it is found that the large-N approximation is also a lower-bound to the exact energy but that this bound is even weaker than that for convex-Coulomb potentials. It will be shown in chapters 3 and 4 that a similar comparison between the *JWKB* approximation and the method of potential envelopes is not possible at the present time.

CHAPTER 3
THE JWKB APPROXIMATION

3.1 History

Among the many different approximation techniques developed for solving differential equations, the *JWKB* method stands out as one of the oldest, most powerful and most elegant. It has found application in almost every major field of modern physics, and continues to do so today. A voluminous literature exists on the subject.

The method is named after some of the major contributors to the theory in the twentieth century: Jeffreys[20] (1923), Wentzel[21] (1926), Kramers[22] (1926), and Brillouin[23] (1926). It is also known under various other names: the L.R. approximation, after Liouville[24] (1837) and Rayleigh[25] (1912), the WKB approximation, the semi-classical approximation or the phase-integral method[26]. Due to the historical development, some of these titles have troubled some authors, for instance Bailey[27] has written: *"The custom, based on historical ignorance, of using the titles 'B.K.W.' or 'W.K.B.' (or some other permutation of these three letters) is wrong as it*

does such flagrant injustice to the truth." As a result of the widespread usage of the label *'WKB'* however, we will simply employ the title *JWKB* which makes additional reference to Jeffreys' contribution.

Solutions of *JWKB* form (known as asymptotic solutions for reasons to be discussed below) were used as far back as 1817 by Carlini[26] who solved approximately what is today known as Bessel's equation. Liouville[24] and Green[28] considered more general equations and found approximate solutions for them in similar fashion. In this century many workers have made contributions to the theory. In 1912 Rayleigh[25] published a paper which dealt with the propagation of waves through a medium with varying index of refraction; his approximate solution to the equation involved in this investigation has a form very similar to that of one of the standard *JWKB* solutions in use today (eqn. (3.15) below). Jeffreys, in 1923, was the first to standardize the *JWKB* solutions. This was accomplished during his investigations of approximate solutions to Mathieu's equation, which he had applied to the study of the free oscillations of water in an elliptical lake[20].

During the early years of the quantum theory much attention was devoted to obtaining solutions of Schrödinger's equation. Approximate solutions were essential and the *JWKB* method was one of the important techniques applied to the problem. Wentzel[21] and

Kramers[22] did the pioneering work in this area. Both studied eigenvalue problems and problems dealing with potential wells. In 1928 Gamow and, independently, Gurney and Condon derived the transmission coefficient for the penetration of the potential barrier of a nucleus by an alpha particle using *JWKB* theory[29]. Other important applications have included the propagation of electro-magnetic waves in the atmosphere[30] and acoustical diffraction in inhomogeneous media[31]. Certain historical references are best presented in the context of a theoretical development and will be cited below. A more comprehensive historical review may be found in the book by Heading[26].

In the next section we present an exposition of the theory behind the *JWKB* approximation.

3.2 *JWKB* theory

It is interesting to note that for an approximation method with such a long history some controversy still exists regarding its mathematical foundations. This has caused Heading[26] to comment: "*...it is surprising that the development of this technique has been the occasion of so much error, criticism and dispute.*" In the present discussion we will only elucidate the less contentious

aspects of the theory. Any attempt to do otherwise and do justice to the difficulties involved would require an in-depth investigation, which is beyond the scope of this thesis.

The *JWKB* approximation can most comfortably be applied in quantum mechanics to problems where the Schrödinger equation involves a single variable. This occurs when: (*i*) we deal with one dimensional problems or, (*ii*) the potential under scrutiny is spherically symmetric, and it is possible to separate out a radial differential equation. We will study these cases individually since each presents its own set of problems.

3.2.1 The *JWKB* approximation in $\mathbb{R}$

For this first case, we have adapted the presentations of Bransden and Joachin[29] and that of Merzbacher[32] for our discussion. The central result that will emerge from this investigation is a relationship between the potential and the eigenvalues of the particular Hamiltonian under scrutiny (eqn. (3.38)). As a result, for potentials satisfying certain criteria, it will be possible to calculate approximate eigenvalues.

Consider the one-dimensional Schrödinger equation

$$\left[\frac{d^2}{dx^2} + \frac{2m}{\hbar^2}(E - V)\right]\psi(x) = 0. \tag{3.1}$$

The solution to this differential equation is trivial if $V = V_o$ is a constant; for this special case the solutions are plane waves $\psi = e^{\pm ikx/\hbar}$, where k is the constant

$$k = \left[2m(E - V_o)\right]^{1/2}. \tag{3.2}$$

Thus, if instead V is a slowly varying function of x, it is reasonable to assume that the real and imaginary parts of ψ will still oscillate as plane waves. This assumption should at least be valid in an interval that is small relative to the distance over which $V(x)$ varies noticeably. The de Broglie wavelength is then position dependent and given locally by the relation

$$\lambda(x) = \frac{2\pi\hbar}{k(x)} = \frac{2\pi\hbar}{\left\{2m\left[E - V(x)\right]\right\}^{1/2}}. \tag{3.3}$$

Under such conditions we may adopt the same plane wave form for ψ with a more complex functional form for the exponent[29,32]

$$\psi(x) = e^{iS(x)/\hbar}, \tag{3.4}$$

where $S(x)$ is *not* a linear function of x. To simplify the

notation the following definitions will be assumed

$$k(x) = \left\{2m[E - V(x)]\right\}^{1/2} \quad \text{if} \quad E > V(x), \tag{3.5a}$$

$$k(x) = -i\left\{2m[V(x) - E]\right\}^{1/2} = -ik(x) \quad \text{if} \quad E < V(x). \tag{3.5b}$$

Equation (3.5a) is the classical momentum of a particle at position x. The problem of solving (3.1) now shifts to finding an explicit expression for the function $S(x)$. We substitute (3.4) into (3.1) and find that $S(x)$ satisfies

$$i\hbar\frac{d^2S}{dx^2} - \left(\frac{dS}{dx}\right)^2 + [k(x)]^2 = 0. \tag{3.6}$$

The Schrödinger equation has thus been transformed into (3.6). This new equation is obviously nonlinear and therefore even more complicated to solve than Schrodinger's equation. It is this nonlinearity, however, that allows the approximation scheme of the *JWKB* method to succeed[32]. We now outline how an approximate solution to (3.6) can be found. For the case V = constant, we have, $S'' = 0$ ($S(x) = \pm kx$, see (3.2)). Also, in the classical limit, $\hbar \longrightarrow 0$, the first term of (3.6) drops out. So the classical limit reproduces the result for $S(x)$ in this case (when V = constant). Therefore, when the potential is not

constant but is slowly varying we can consider expressing $S(x)$ as a power series expansion in which $\hbar$ is the expansion parameter. Thus:

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + O(\hbar^3). \tag{3.7}$$

Such series solutions to differential equations are known as *asymptotic series;* They possess the rather special property that although they represent the function in question they are *divergent*. To place this statement on a more quantitative footing consider the partial sum of the series (3.7)

$$\varphi_n(1/\hbar) = \sum_{\nu=0}^{n} \frac{S_\nu(x)}{(1/\hbar)^\nu}. \tag{3.8}$$

If for the moment we think of $\hbar$ as a variable then for fixed $(1/\hbar)$ and $n \longrightarrow \infty$ we have $\varphi_n(1/\hbar) \longrightarrow \infty$ but for fixed n and $(1/\hbar) \longrightarrow \infty$ the sum $\varphi_n(1/\hbar)$ gives an increasingly accurate approximation to the function $S(x)$; that is,

$$\lim_{z\to\infty} z^n[\varphi_n(z) - S(z)] = 0, \tag{3.9}$$

where $z = 1/\hbar$ and we have considered S as a function of $1/\hbar$. Due to the fact that the series φ_n diverges for $n \longrightarrow \infty$ there is an optimum number of terms which best represents $S(x)$. Since $1/\hbar$ is a very large number and we will be considering

only a finite number of terms of the series (3.7), it is reasonable to assume that this expansion will represent $S(x)$ adequately. Horn[33] was the first investigator to analyze asymptotic series associated with solutions of differential equations. A lucid introduction to the theory of asymptotic series can be found in Wittaker[34]. The very interesting text by the Russian author Midgal contains a similar presentation at a slightly lower level of sophistication[35].

Feeding (3.7) into (3.6) and neglecting terms of $O(\hbar^3)$ implies

$$\left\{[S_o']^2 - [k(x)]^2\right\} + \left\{2S_o'S_1' - iS_o''\right\}\hbar + \left\{2S_o'S_2' + [S_1']^2 - iS_1''\right\}\hbar^2 = 0. \tag{3.10}$$

Equating the coefficients of the various powers of $\hbar$ we obtain

$$[S_o']^2 - [k(x)]^2 = 0, \tag{3.11a}$$

$$2S_o'S_1' - iS_o'' = 0, \tag{3.11b}$$

$$2S_o'S_2' + [S_1']^2 - iS_1'' = 0. \tag{3.11c}$$

Solving these equations successively, results in the various orders of approximation to $S(x)$. The zeroth order is given

by the solution of (3.11a)

$$S_0 = \pm \int^x k(x)dx. \tag{3.12}$$

The second term ($S_1(x)$) in the expansion (3.7) can then be evaluated by making use of (3.11b), and (3.12), namely

$$S_1(x) = \frac{i}{2} log[k(x)]. \tag{3.13}$$

Lastly, by substituting (3.12) and (3.13) into (3.11c), an expression for $S_2(x)$ is obtained

$$S_2(x) = \frac{mV'(x)}{4k^3(x)} - \frac{m^2}{8}\int^x \frac{[V'(x)]^2}{k^5(x)}dx. \tag{3.14}$$

S_2 will be negligible if V' is small, assuming that $|E - V|$ is not too close to zero. Also, if all higher derivatives of $V(x)$ are small, then all higher order terms in the series may safely be neglected.

In the *JWKB* approximation all terms in the series for $S(x)$ of higher order than the first are neglected. When substituted into (3.4) equations (3.12) and (3.13) result in the 1st order *JWKB* approximation to the wave function

$$\psi(x) \simeq \frac{1}{[k(x)]^{1/2}} exp\left[\pm \frac{i}{\hbar}\int^x k(x)dx \right], \tag{3.15}$$

where it is to be understood that the general solution to

(3.1) is a linear combination of each of the waves implied by the symbol ± in (3.15), one travelling to the left and the other to the right.

How well (3.15) approximates the true wave function depends on the extent to which neglecting higher order terms in the series (3.7) is justified. As stated above, the condition that should be satisfied is

$$|\hbar^2 S_2(x)| \ll 1. \tag{3.16}$$

That is, the third term in the series should be negligible. Making use of the first term of eqn. (3.14), implies that (3.16) can be expressed as

$$\left| \frac{\hbar m V'(x)}{\left\{ 2m[E - V(x)] \right\}^{1/2}} \right| \ll 1. \tag{3.17}$$

The second term of eqn. (3.14) is of the same order of magnitude, therefore it can be neglected in the present discussion. Equation (3.17) can also be expressed in a more physically revealing manner, namely

$$\left| \frac{\hbar k'(x)}{k(x)} \right| = \lambda\!\!\!^{-}(x) \left| \frac{dk}{dx} \right| \ll |k(x)|, \tag{3.18}$$

with $\lambda\!\!\!^{-}(x) = \hbar/k(x) = \lambda(x)/2\pi$ (the reduced de Broglie wavelength). The right-hand side of this equation tells us

that for (3.15) to be a good approximation, the change in momentum of the particle within one wavelength, must be small compared to the momentum itself[32]. What this implies is that the potential must change slowly enough so as not to alter the momentum very much over an interval of many wavelengths.

3.2.1.1 The connection formulae

Condition (3.18) will *not* hold if either one of two situations exist, (*i*) the potential changes very quickly, or (*ii*) k(x) vanishes. The second case will occur wherever

$$V(x) = E. \tag{3.19}$$

A value of x which satisfies (3.19) is known as a *classical turning point* (or transition point), for obvious reasons (see fig.3.1). The *JWKB* solutions do not apply near such turning points. As can be deduced from (3.15), ψ is singular when k(x) = 0. However, we know that the true wave function does exist at a turning point. This implies that some way must be found of taming the *JWKB* function at this point so as to connect the two approximate *JWKB* solutions which exist to the left and right of it. Gans[36] (1915) seems to have been the first worker to resolve this dilemma. His contribution was to replace the true potential $V(x)$ by a

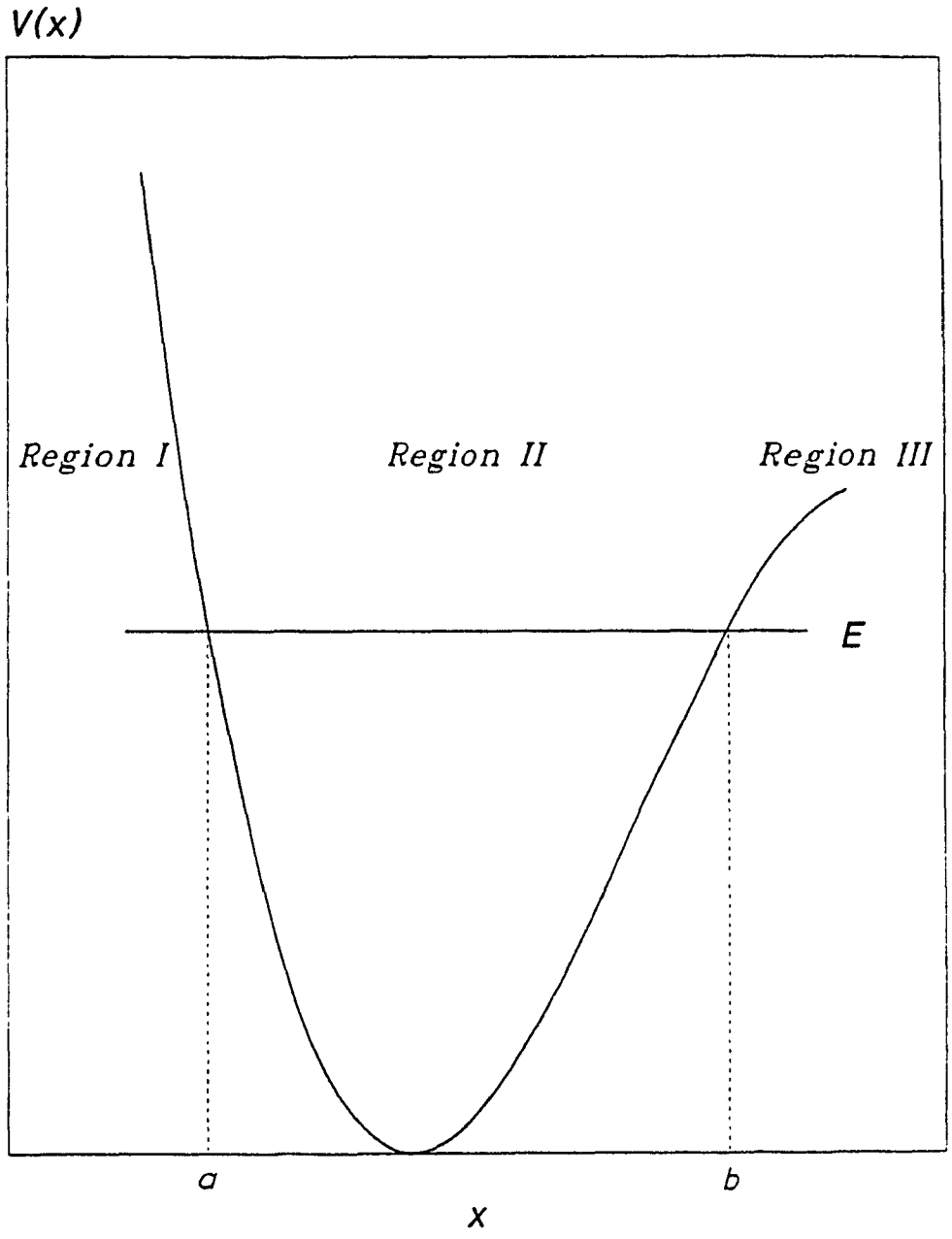

Fig.3.1 Turning points for a given potential V and energy E.

linear approximation derived from a second order Taylor expansion. This is a reasonable step since we are assuming throughout that $V(x)$ varies only slowly with x. A solution of the Schrödinger equation is thus obtained which contains no singularity at the turning point, all three solutions are then patched together to produce a global solution. The expressions arising out of this procedure of matching the solutions on either side of a turning point are known as the *connection formulae*. It is from these relations that an expression for the eigenvalues of a potential well can be developed. We now derive the connection formulae.

Consider a turning point lying to the left of the classical region (fig.3.1). In the neighborhood of the turning point $x = a$ we write

$$k^2(x) \simeq \alpha(x - a), \qquad \alpha = \left[\frac{dk^2(x)}{dx}\right]_{x = a}, \tag{3.20}$$

with $\alpha > 0$. By defining a new independent variable ζ as follows

$$\zeta(x) = (\hbar^2\alpha)^{1/3}(x - a), \tag{3.21}$$

and then substituting (3.20) and (3.21) into the Schrödinger

equation (3.1) we get:

$$\left[\frac{d^2}{d\zeta^2} + \zeta \right] \Psi(\zeta) = 0, \tag{3.22}$$

where $\Psi(\zeta(x)) = \psi(x)$, is just the wave function expressed in terms of the variable ζ. Equation (3.22) is the Airy equation which has the general solution[37]

$$\Psi(\zeta) = c_1 Ai(-\zeta) + c_2 Bi(-\zeta), \tag{3.23}$$

where c_1, c_2 are arbitrary constants. The functions $Ai(-\zeta)$ and $Bi(-\zeta)$, known as the Airy functions, have simple expressions for large and small values of ζ. These asymptotic forms are as follows:

If $Ai(-\zeta)$ is bounded and oscillatory then,

$$\begin{aligned} Ai(-\zeta) &\sim \pi^{-1/2}\zeta^{-1/4}\cos\left(\frac{2}{3}\zeta^{3/2} - \frac{\pi}{4}\right), && \zeta \longrightarrow \infty \\ &\sim \frac{1}{2}\pi^{-1/2}|\zeta|^{-1/4}\exp\left(-\frac{2}{3}|\zeta|^{3/2}\right), && \zeta \longrightarrow -\infty. \end{aligned} \tag{3.24}$$

If $Bi(-\zeta)$ is unbounded in the limit $\zeta \longrightarrow -\infty$ we have,

$$Bi(-\zeta) \sim \pi^{-1/2}\zeta^{-1/4}\sin\left(\frac{2}{3}\zeta^{3/2} - \frac{\pi}{4}\right), \qquad \zeta \longrightarrow \infty$$

$$\sim \frac{1}{2}\pi^{-1/2}|\zeta|^{-1/4}\exp\left(\frac{2}{3}|\zeta|^{3/2}\right). \qquad \zeta \longrightarrow -\infty. \tag{3.25}$$

We will now show that (3.22) is an approximation to the Schrödinger equation (3.1) not only near a turning point but in fact, $\forall x \in \mathbb{R}$, thus the approximate solution (3.23) holds for all values of x. A comparison of the *JWKB* solutions for (3.22) and the *JWKB* solutions of the original schrödinger equation shows that $\psi(x)$ can be approximated by

$$\tilde{\psi} = \left[\frac{\hbar^2\zeta(x)}{k^2(x)}\right]^{1/4}\Psi(\zeta(x)), \tag{3.26}$$

with $\zeta(x)$ defined as

$$\frac{2}{3}[\zeta(x)]^{3/2} = \frac{1}{\hbar}\int_a^x k(x)dx, \qquad k^2 > 0 \tag{3.27a}$$

$$= e^{\pm 3\pi i/2}\,\frac{1}{\hbar}\int_a^x \kappa(x)dx, \qquad k^2 < 0. \tag{3.27b}$$

Due to the fractional powers a phase factor appears in (3.27b). This has been chosen such that $\mathrm{im}(\zeta) = 0$ and $\zeta < 0$ for $k^2 < 0$. By substituting (3.26) into (3.22), we find

that $\tilde{\psi}$ satisfies the equation:

$$\left[\frac{d^2}{dx^2} + \hbar^{-2}k^2(x) + \varepsilon(x) \right]\tilde{\psi}(x) = 0, \tag{3.28}$$

where

$$\varepsilon(x) = -\left(\frac{d\zeta}{dx} \right)^{1/2} \frac{d^2}{dx^2} \left\{ \left| \frac{d\zeta}{dx} \right|^{-1/2} \right\}. \tag{3.29}$$

If the third term in (3.28) is negligible, that is

$$|\hbar^2\varepsilon(x)/k^2(x)| \ll 1, \tag{3.30}$$

then the function $\tilde{\psi}(x)$ is a good approximation to $\psi(x)$. We are now in a position to demonstrate that $\tilde{\psi}(x)$ is indeed an approximate solution to the Schrodinger equation $\forall x \in \mathbb{R}$ (with $\Psi(\zeta(x))$ given by (3.23)). When $\varepsilon(x) = 0$, (3.28) is identical with the Schrödinger equation, this occurs at a turning point. Also, far from such a point condition (3.30) is a weaker bound than (3.17)[29], which is the criterion of validity for the *JWKB* approximation (3.15). Therefore (3.26) is equivalent to the *JWKB* solutions far from a turning point and solves the Schrödinger equation exactly in the neighborhood of and at a turning point.

For a solution to be bounded to the left of a turning point the second term in the linear combination (3.23) must be set to zero since this solution diverges in this

interval: thus $c_2 = 0$. The wave function can then be expressed $\forall x \in \mathbb{R}$ as

$$\psi(x) \simeq c_1 \left[\frac{\hbar^2 \zeta(x)}{|k^2(x)|} \right]^{1/4} Ai(-\zeta(x)). \tag{3.31}$$

We have therefore succeeded in matching the *JWKB* solutions across the turning point. Employing equations (3.24) and (3.27) the connection formulae are[32]

$$\left[k(x)\right]^{-1/2} exp\left(- \frac{1}{\hbar}\int_x^a k(x)dx \right) \longrightarrow$$

$$2\left[k(x)\right]^{-1/2} cos\left(\frac{1}{\hbar}\int_a^x k(x)dx - \frac{\pi}{4} \right), \tag{3.32a}$$

$$\left[k(x)\right]^{-1/2} sin\left(\frac{1}{\hbar}\int_a^x k(x)dx - \frac{\pi}{4} \right)$$

$$-\left[k(x)\right]^{-1/2} exp\left(\frac{1}{\hbar}\int_x^a k(x)dx \right) \longleftarrow . \tag{3.32b}$$

There exist two cases to be considered corresponding to (3.32a) and (3.32b) respectively:

(*i*) If the *JWKB* solution is known to decay exponentially in the limit $x \longrightarrow -\infty$, then (3.32a) is the correct connection

formula to use. The left-hand side applies in the interval $x < a$ and the right-hand side in the interval $x > a$.

(*ii*) On the other hand if the wave function increases exponentially to the left of the turning point then (3.32b) is the appropriate form.

The above analysis assumes that we are dealing with a potential barrier which lies to the left of a turning point. If however the barrier is to the right of the turning point then the connection formulae are altered and become:

$$\left[k(x)\right]^{-1/2} exp\left(- \frac{1}{\hbar}\int_{b}^{x} k(x)dx \right) \qquad (3.33a)$$

$$2\left[k(x)\right]^{-1/2} cos\left(\frac{1}{\hbar}\int_{x}^{b} k(x)dx - \frac{\pi}{4}\right) \longleftarrow ,$$

and

$$\left[k(x)\right]^{-1/2} sin\left(\frac{1}{\hbar}\int_{x}^{b} k(x)dx - \frac{\pi}{4} \right) \longrightarrow \qquad (3.33b)$$

$$-\left[k(x)\right]^{-1/2} exp\left(\frac{1}{\hbar}\int_{b}^{x} k(x)dx \right),$$

with qualifications similar to (*i*) and (*ii*) applying in each

case. The particular forms of (3.32) and (3.33) were first set out by Jeffreys in 1923[20]. This work was accomplished without knowledge of Gans' earlier work[26]. Much of the controversy associated with *JWKB* theory results from differing opinions as to the proper interpretation of the unidirectional nature of (3.32) and (3.33)[38] (arrow symbols). The arrows indicate *the direction in which these formulae should be applied*. For instance, consider the case of a potential barrier lying to the left of the turning point; if we know that for $x < a$ the correct approximate representation to the exact solution is one of exponential growth we *cannot* assume that for $x > a$ the sine represents ψ satisfactorily. The exact solution may contain an exponentially decreasing component which would be negligible to the far right of the turning point but which might result in a substantial admixture of cosine to the right of the turning point, according to (3.33a). A similar argument can be made against employing (3.33a) in the wrong direction. Of course, if we can ascertain that the wave function is composed of only one linearly independent component (e.g. either *only* an exponentially decreasing or *only* an exponentially increasing component exists far to the left or far to the right of the turning point) then the above argument does not apply[32].

3.2.1.2 *JWKB* quantization condition for bound states

The *JWKB* approximation has many applications. As mentioned above however our main interest in discussing this technique is in connection with the approximation of the eigenenergies of bound states. For simplicity we will consider a potential well with only two turning points. Approximate solutions of *JWKB* form can immediately be written down for each of the three regions indicated in fig.3.1. Solutions which increase exponentially for $x < a$ or $x > b$ must eventually vanish since ψ must be finite. Thus, the appropriate *JWKB* solution in region I is

$$\psi_I \simeq \left[k(x)\right]^{-1/2} \exp\left(- \frac{1}{\hbar}\int_x^a k(x)dx \right), \quad \text{for } x < a. \tag{3.34}$$

The connection formula (3.33a) automatically provides us with the solution in region II

$$\psi_{II} \simeq 2\left[k(x)\right]^{-1/2} \cos\left(\frac{1}{\hbar}\int_a^x k(x)dx - \frac{\pi}{4} \right), \quad \text{for } a < x < b. \tag{3.35}$$

By a bit of algebraic manipulation it can be shown that

$$\psi_{II} \simeq -2\left[k(x)\right]^{-1/2} \cos\left(\frac{1}{\hbar}\int_a^b k(x)dx \right) \sin\left(\frac{1}{\hbar}\int_x^b k(x)dx - \frac{\pi}{4} \right)$$

$$+ 2\left[k(x)\right]^{-1/2} \sin\left(\frac{1}{\hbar}\int_a^b k(x)dx \right) \cos\left(\frac{1}{\hbar}\int_x^b k(x)dx - \frac{\pi}{4} \right). \tag{3.36}$$

However, by (3.33a) the first term does not result in a decreasing exponential and it must therefore vanish in order that the wave function satisfy the boundary condition at infinity. This results in the expression which we have been seeking

$$\frac{1}{\hbar}\int_a^b k(x)dx = \left(n - \tfrac{1}{2}\right)\pi , \qquad n = 1,2,3,..., \tag{3.37}$$

or more explicitly

$$\frac{1}{\hbar}\int_a^b \left\{2m\left[E - V(x)\right]\right\}^{1/2} dx = \left(n - \tfrac{1}{2}\right)\pi , \qquad n = 1,2,3,... . \quad (E > V) \tag{3.38}$$

The *JWKB* method thus provides a means of approximating the eigenvalues for a given potential. Note that the discrete energies E appear not only in the integrand but also in the limits of integration (e.g. $V^{-1}(E) = a$). This makes for a

rather interesting problem when it comes to evaluating the eigenvalues numerically. In deriving (3.38) we have implicitly assumed that the potential at all times varies smoothly. If the potential is an infinite square well with walls at a and b or if it suffers an infinite discontinuity at these points then this condition must be altered[39]. The correct recipe being

$$\frac{1}{\hbar}\int_a^b \left\{2m\left[E - V(x)\right]\right\}^{1/2} dx = n\pi \ , \qquad \begin{matrix} n = 1,2,3,\ldots \ . \\ (E > V) \end{matrix} \tag{3.39}$$

Since *JWKB* theory is a semi-classical theory ($\hbar \longrightarrow 0$) we expect that the eigenvalues E derived from (3.38) will be good approximations to the exact energies for large values of the quantum number n. We will show in chapter 4 that the *JWKB* eigenvalues are indeed very good approximations to the energies.

There also exists a relationship between *JWKB* and the old quantum theory. According to the Bohr-Sommerfeld quantization rules[32]

$$\oint p_i dq_i = (n_i - 1)h, \tag{3.40}$$

where p_i, q_i are respectively the generalized momenta and coordinates. The integral is evaluated over a complete

period of the coordinate q_1. Rearranging (3.37) we obtain

$$\oint p(x)dx = \left(n - \tfrac{1}{2}\right)h, \tag{3.41}$$

where $p(x) = k(x)$ is the classical momentum. The extra term of $h/2$ in (3.41) provides for the zero-point energy, which (3.40) lacks.

The left-hand side of (3.41) represents the change in phase of ψ_{II} from a to b. We can easily show that as a result, $\frac{1}{2}n + \frac{1}{4}$ wavelengths (quasi-wavelengths) fit between a and b; n thus represents the number of nodes the wave function contains.

Surprisingly, the spectrum of the harmonic oscillator potential is *exactly* reproduced by (3.38), this feature persists in the three-dimensional *JWKB* approximation. In addition, for the $\mathbb{R}^3$ case to be discussed below, with $V(x)$ representing the hydrogenic atom, the *JWKB* approximation once again produces the exact spectrum. This would seem not to be a coincidence. In fact, a rather deep connection exists between the two problems[40].

For general $V(x)$ it is not possible to evaluate exactly the integral occurring in (3.38) . One important exception to this rule is the case of symmetric power-law potentials

$$V(x) = \beta|x|^q \ , \quad \beta > 0, \ q > 0. \tag{3.42}$$

Sukhatme[41] has shown that in this case the integral can be

performed exactly and results in

$$E_n = \left\{ \frac{\left(n - \frac{1}{2}\right)\hbar\beta^{1/q}\Gamma\left(\frac{3}{2} + q^{-1}\right)}{4(2m)^{1/2}\Gamma\left(\frac{3}{2}\right)\Gamma\left(1 + q^{-1}\right)} \right\}^{2q/(q+2)}. \tag{3.43}$$

3.2.2 The *JWKB* Approximation in $\mathbb{R}^3$

For problems in $\mathbb{R}^3$ where separation of the variables is possible, the radial part of the Schrodinger equation may be expressed in the following form

$$\frac{d^2u_\ell}{du_\ell^2} + W^2(r)u_\ell = 0, \tag{3.44}$$

with

$$W^2(r) = \frac{1}{\hbar^2}\left(k^2 - \frac{\ell(\ell + 1)}{r^2} \right), \qquad k^2 = 2m\left[E - V(r)\right], \tag{3.45}$$

where u_ℓ is the radial part of the wave function. Equation (3.44) will take on a form identical to the one-dimensional Schrodinger equation if one makes the identification

$$\tilde{V}(r) \equiv V(r) + \frac{\ell(\ell + 1)\hbar^2}{2mr^2}. \tag{3.46}$$

Thus $\tilde{V}$ can be considered an effective potential. As a result, *for potentials which are finite at the origin* the

JWKB quantization condition for $\ell > 0$ in $\mathbb{R}^3$ is almost identical to that in $\mathbb{R}$ (eqn.(3.38)) and is given by

$$\int_{r_{min}}^{r_{max}} \left\{ 2m\left[E - V(r) - \frac{(\ell + 1/2)^2}{2mr^2}\right]\right\}^{1/2} dr = \left(n - \frac{1}{2}\right)\pi\hbar \ , \qquad n = 1,2,3,\ldots, \tag{3.47}$$

here n is the principal quantum number in three-dimensions and r_{min}, and r_{max} are defined by $V(r_{min}) = V(r_{max}) = E$[35]. Also, the centrifugal term in this equation has been altered; that is, we have replaced the quantity $\ell(\ell + 1)$ by $(\ell + 1/2)^2$, this is known as the Langer correction[35]. If this is not done the criterion of applicability (3.17) will not be fulfilled near the origin and the *JWKB* solution will not be valid. This change in the centrifugal term has a negligible effect on the energies[35]. When dealing with *S*-states of potentials which exhibit a singularity at the origin, the right hand side of the quantization condition must be modified to compensate for the left-hand turning point. For such cases this point now coincides with the singularity. The correct equation is

$$\int_{0}^{r_{max}} \left\{ 2m\left[E - V(r)\right]\right\}^{1/2} dr = n\pi\hbar \ , \qquad n = 1,2,3,\ldots \ . \tag{3.48}$$

For the special case of power-law potentials (eqn.(3.42)

with x everywhere replaced by r) closed form solutions once again exist for all values of the angular momentum quantum number ℓ. For potentials which are finite at the origin these solutions can be expressed as follows[39]

$$E_n = \beta^{2/(2+q)} (2m/\hbar^2)^{-q/(2+q)} \left[A(q) \left(n + \frac{\ell}{2} - \frac{5}{4} \right) \right]^{2q/(2+q)}$$

where (3.49)

$$A(q) = \left[2q\sqrt{\pi}\ \Gamma\left(\frac{3}{2} + 1/q \right) \right] \Big/ \Gamma(1/q) \ , \qquad q > 0.$$

For potentials which are singular at the origin exact solutions of (3.48) are also forthcoming and are given by

$$|E_{n\ell}| = |\beta|^{2/(2+q)} (2m/\hbar^2)^{-q/(2+q)} \times \left\{ \tilde{A}(q) \left[n - 1 + \frac{1}{2} \left(\frac{1 + q - 2\ell}{2 + q} \right) \right] \right\}^{2q/(2+q)},$$

$$\tilde{A}(q) = \left[2|q|\sqrt{\pi}\ \Gamma\left(1 - 1/q \right) \right] \Big/ \Gamma\left(-\frac{1}{2} - \frac{1}{q} \right), \quad -2 < q < 0,$$

(3.50)

which holds $\forall \ell$[39]. As was stated above, this expression is exact for the Coulomb potential.

In this dissertation we have considered three different schemes for approximately solving bound-state eigenvalue problems in quantum mechanics. As an illustration of these

various approximation techniques in action and as a comparison of their results, in the following chapter we apply two of these techniques to a single fixed potential. Thus approximate numerical results are obtained for the eigenenergies of the Coulomb-plus-Yukawa potential via: the method of potential envelopes, and the *JWKB* approximation.

3.3 Improvements to the 1st order *JWKB* Approximation

In §3.2 the derivation of the quantization condition for the energies E (eqn.(3.38)) was predicated on the truncation of the asymptotic series (3.7) after the first two terms. This first order approximation has been improved upon by a number of workers. Dunham[42] was the first to extend the theory beyond the 1st order; he obtained the second and third nonzero terms in the *JWKB* quantization condition. As an application of the three-term theory Krieger *et al.*[43] explored the eigenvalues of potentials with form $V(x) = \lambda x^{2\nu}$. Two groups of investigators; Kesarwani and Varshni[44] and independently Kirschner and LeRoy[45] have studied the Lennard-Jones potentials with the three-term approximation. Expressions for the four-term and the five-term *JWKB* quantization conditions respectively have been derived by Kesarwani and Varshni[46]. Unfortunately, the complexity of the resulting formulae grows quickly as

more terms are kept, involving not only V itself but also higher derivatives. It is not at all clear that numerical calculations would not be more efficient in most cases.

Many other improvements have been made over the years, from the generalization of the theory[47], to the establishment of error bounds[38,48-50].

3.4 *JWKB* scaling laws

Scaling arguments can be applied to the *JWKB* quantization condition as they were to the Schrodinger equation in Chapter 1. The question of *JWKB* scaling has not been dealt with in the liturature before. The benefits of such a procedure are twofold:

(*i*) elimination of the clutter which obscures the main aspects of the theory,

(*ii*) from a practical perspective scaling simplifies the calculations and improves the accuracy in any numerical investigation.

Consider the one-dimensional Schrödinger equation in the form of chapter 1, that is

$$\left[-D^2 + v f(x)\right]\psi = E(v)\psi, \tag{3.51}$$

with $V(x) = V_0 f(x/a)$, $V_0 > 0$, $a > 0$ and $f(-x) = f(x)$ $\forall x$ and monotone increasing on the interval $(0,\infty)$. The *JWKB* quantization condition (3.38) can be rewritten in a simpler form if the factor $2m/\hbar^2$ is absorbed, namely

$$W(\mathcal{E}) = \int_{-f^{-1}(\mathcal{E})}^{f^{-1}(\mathcal{E})} \left[\mathcal{E}(v) - v f(x)\right]^{1/2} dx = \left(n - \tfrac{1}{2}\right)\pi, \quad n = 1,2,3,\ldots \quad (\mathcal{E} > f) \tag{3.52}$$

where $\mathcal{E}(v) = (2ma^2/\hbar^2)E(v)$, $v = 2mV_0a^2/\hbar^2$ is the *JWKB* approximation to the eigenvalue. $W(\mathcal{E})$ is monotone increasing, therefore W^{-1} exists. It is then easy to show that the dependence of $\mathcal{E}$ on the coupling constant v is

$$\mathcal{E}(v,n) = vW^{-1}\left[\frac{\pi(n - 1/2)}{(va^2)^{1/2}}\right]. \tag{3.53}$$

When $f(x)$ is a power-law potential with form $sgn(q)|x|^q$, $q \neq 0$, the scaling law has a very simple form:

$$\mathcal{E}(v) = \mathcal{E}(1)v^{2/(2+q)}. \tag{3.54}$$

Thus, we see that all we need to establish how $\mathcal{E}$ relates to the coupling constant is to know the approximate *JWKB* eigenvalue $\mathcal{E}(1)$. It is interesting to note that this is the same scaling law that applies to the Schrodinger equation for power-law potentials[51]. Also the dependence of W on ω can be shown to be

$$W(\omega) = W(1)\omega^{(q+2)/2q} \quad . \tag{3.55}$$

3.5 Error bounds on *JWKB* eigenvalues

An important consideration for any approximation scheme is the possibility of establishing error bounds. In relationship to the *JWKB* solutions this has been a problem of concern to a number of researchers[26,38,48-50].

Of particular interest in the present context is the work of Birx and Houk[48]. They have developed a means of obtaining upper and lower bounds to the exact energies $\mathcal{E}_n$ by employing the *JWKB* quantization condition (3.38). Their technique centers on the simple fact that the amount by which $\mathcal{E}_n$ is under or overestimated by (3.38) is determined by how much $k(x)$ is under or overestimated (see eqn. (3.37)). If we can set limits on these upper and lower values, then upper and lower bounds to the energies can be obtained.

It is the shape of the wave function that leads to this uncertainty in $k(x)$, since for a given state the quasi-wavelength $\lambda(x)$ of the wave function is related to $k(x)$ through $k(x) = 2\pi\hbar/\lambda(x)$. This means that a wave function with a given number of nodes, which does not penetrate into the classically forbidden region, will possess the shortest possible wavelength for an oscillatory solution in the region $\mathcal{E}_n > V(x)$. Such a constraint on ψ implies that k takes on its maximum value, resulting in an upper bound for k and consequently for $\mathcal{E}_n$. For this to be the case the potential can be of only one form

$$\begin{aligned} V &= \infty \ , \qquad x < a \text{ or } x > b, \\ V &= V(x) \ , \qquad a < x < b, \end{aligned} \tag{3.56}$$

thus ψ must vanish at the turning points. In §3.2.1.2 (eqn.(3.39)) we have already discussed how such a boundary condition modifies the quantization condition

$$(3.39) \longrightarrow \int_a^b \left[\mathcal{E} - f(x)\right]^{1/2} dx = n\pi = \mathcal{G}_2(n) \ , \qquad n = 1,2,3,... \tag{3.57}$$

where the form introduced in §3.4 has been employed for the LHS with $\upsilon = 1$, implying, $\mathcal{E}(\upsilon) = \mathcal{E}(1)$.

How far can the wave function penetrate into the classically forbidden region? The answer to this question

dictates the maximum *underestimation* of k and therefore establishes a lower bound on k and on $\mathcal{E}_n$, the true energy. Inspecting the Schrödinger equation we see that ψ must be approaching the x axis on the forbidden side of the turning point for the standard boundary condition at infinity, $\int_{-\infty}^{+\infty} \psi^* \psi dx < \infty$, to apply. For the extreme case this means that, $|\psi'|_{x=a,b} \simeq 0$. Of course, this limit can never be attained, since for $\psi' = 0$, ψ itself must vanish everywhere. However, it is still legitimate to utilize this limiting boundary condition to derive our lower bound and doing so results in a new quantization condition:

$$(3.38) \longrightarrow \int_a^b \left[\mathcal{E} - f(x)\right]^{1/2} dx = (n-1)\pi = \mathcal{G}_3(n), \qquad n = 1,2,3,... \tag{3.58}$$

Equations (3.57) and (3.58) produce upper and lower bounds respectively to $\mathcal{E}_n$.

We can go one step further and demonstrate that these bounds are tight enough to exclude all other adjoining eigenvalues. To see this let us express $\mathcal{E}_n$ as a power series in $\mathcal{G}_i(n)$

$$\mathcal{E}_n = \sum_{\nu} c_\nu \mathcal{G}_i^\nu(n), \tag{3.59}$$

where $\mathcal{G}_1 = (n - 1/2)\pi$ refers to the original quantization

condition (3.38). For three neighboring eigenvalues that are ordered as

$$\varepsilon_{n-1} < \varepsilon_n < \varepsilon_{n+1}, \tag{3.60}$$

we examine the *lower bounds* for ε_n, ε_{n+1} and the *upper bounds* for ε_n, ε_{n-1}. Employing the above notation we have, respectively

$$\varepsilon_n^{\ell} = \sum_{\nu} c_{\nu}\left[(n-1)\pi\right]^{\nu}, \qquad \varepsilon_{n+1}^{\ell} = \sum_{\nu} c_{\nu}(n\pi)^{\nu}$$

$$\varepsilon_n^{u} = \sum_{\nu} c_{\nu}(n\pi)^{\nu}, \qquad \varepsilon_{n-1}^{u} = \sum_{\nu} c_{\nu}\left[(n-1)\pi\right]^{\nu}. \tag{3.61}$$

This implies that

$$\varepsilon_{n-1}^{u} = \varepsilon_n^{\ell} < \varepsilon_n < \varepsilon_n^{u} = \varepsilon_{n+1}^{\ell}, \tag{3.62}$$

which proves the above statement.

As an illustration of this result consider the simple harmonic oscillator potential $f(x) = x^2$. The exact solution to this problem is $\varepsilon_n = 2n - 1$, which happens also to be the result produced by the *JWKB* approximation (see §3.3). Table 3.1 shows the upper and lower bounds of Birx's and Houk's theory to the first five eigenvalues ε_n.

Table 3.1 Upper and lower bounds to the exact eigenenergies $\mathcal{E}_n$ of the harmonic oscillator potential $f(x) = x^2$ derived from the *JWKB* approximation by the method of Birx and Houk[48].

n	$\mathcal{E}_n^{\ell}$	$\mathcal{E}_n$	$\mathcal{E}_n^{u}$
1	0	1	2
2	2	3	4
3	4	5	6
4	6	7	8
5	8	9	10

3.6 The connection between potential envelopes and *JWKB*

In chapter 2 it was shown that the existence of a relationship between the Large-N approximation and the theory of potential envelopes made possible comparisons of the results of the two theories. An interesting question then arises, does an analogous connection exist for the *JWKB* method? This was the impetus for our excursion into *JWKB* theory. To date this question remains open. It was discovered by computer exploration that the bounds on the eigenenergies produced by potential envelope theory in its *present form*, are not in general as close to the true energies as the *JWKB* values. This is not to say that future investigations will not alter this situation. But for the present, all we can do is chronicle the progress that has been made.

One possible avenue of approach to the problem is to reformulate the potential envelope inequality (eqn.(1.31)) such that it takes on the form of the *JWKB* quantization condition (3.38). For the purposes of exposition we examine only those potentials which can be represented as concave transformations of the simple harmonic oscillator potential

$$f(x) = g(x^2), \quad g \text{ concave.} \tag{3.63}$$

As was shown in chapter 1, potential envelope theory sets

bounds on the eigenvalues corresponding to such potentials, namely

$$\mathcal{E} \leq \min_{t>0} \left\{ \frac{(n - 1/2)^2}{t^2} + \omega f(t) \right\}, \quad n = 1,2,3,\ldots . \tag{3.64}$$

or

$$\mathcal{E} \leq \frac{(n - 1/2)^2}{t^2} + \omega f(t), \qquad \forall t \in \mathbb{R}^+. \tag{3.65}$$

Rearranging (3.65) we have

$$t\left[\mathcal{E} - \omega f(t)\right]^{1/2} \leq (n - 1/2). \tag{3.66}$$

For what follows it is assumed that, $f(t)$ is symmetric and $f(b) = \mathcal{E}$. To eliminate the factor of t on the LHS of (3.66) we now consider a probability density $\rho(t)$ on $[0,b]$ such that

$$\rho(t) \geq 0, \quad \int_0^b \rho(t)dt = 1, \tag{3.67}$$

which when introduced into (3.66) gives

$$\int_0^b \rho(t)t\left[\mathcal{E} - \omega f(t)\right]^{1/2} dt \leq \int_0^b (n - 1/2)\rho(t)dt = (n - 1/2). \tag{3.68}$$

A possible choice for $\rho(t)$ which satisfies the normalization condition (3.67) is

$$\rho(t) = \begin{cases} 0 , & 0 \le t \le a < b \\ \left[t\ell n(b/a)\right]^{-1} , & a \le t \le b \end{cases} \tag{3.69}$$

Substituting this into (3.68) results in

$$\left(\int_{-b}^{-a} + \int_{a}^{b} \right) \left[\mathcal{E} - v f(t)\right]^{1/2} dt \le 2(n - 1/2)\ell n(b/a) , \tag{3.70}$$

which is equivalent to

$$\int_{-b}^{b} \left[\mathcal{E} - v f(t)\right]^{1/2} dt \le (2n - 1) + 2\frac{b}{e}\mathcal{E}^{1/2} , \tag{3.71}$$

where the parameter a has been fixed by setting $\ell n(b/a) = 1$. The LHS of (3.71) is just the *JWKB* quantization condition (3.38) for a symmetric potential. The *JWKB* condition itself is

$$\int_{-b}^{b} \left[\mathcal{E} - v f(t)\right]^{1/2} dt = (2n - 1)\pi . \tag{3.72}$$

For the case where $f(t)$ is the harmonic oscillator potential, a simple integration results in the following

upper bound to $\mathcal{E}$

$$\mathcal{E} \leq \left(\frac{2e\omega^{1/2}}{\pi e - 4} \right)(2n - 1) \quad n = 1,2,3,\ldots, \tag{3.73}$$

which for $\omega = 1$ gives

$$\mathcal{E} \leq 1.1976(2n - 1) \quad n = 1,2,3,\ldots . \tag{3.74}$$

As mentioned above, the bound on the energies $\mathcal{E}$ is not of much practical use in its present form. Its value is primarily theoretical. It has nevertheless been shown that, in principle, a comparison similar to that achieved between potential envelopes and the Large-*N* approximation in chapter 2 is possible for the *JWKB* method.

CHAPTER 4
NUMERICAL EXAMPLES

In the previous chapters we have explored the theory behind three different approximation methods for solving the Schrödinger eigenvalue problem: the method of potential envelopes, the large-N approximation and the *JWKB* approximation. As a concrete illustration of two of these techniques in action we now apply potential envelope theory and the *JWKB* approximation to a specific problem.

An interesting choice of potential for study is that of the Coulomb-plus-Yukawa potential (CY)

$$V(r) = -\frac{\beta}{r} + \frac{\gamma}{r} e^{-\lambda r} , \quad \beta > 0, \ \gamma < \beta, \ \lambda > 0. \tag{4.1}$$

This potential was the subject of a paper by the present author and Richard Hall[52] (see appendix B) in which the spectrum of the corresponding Schrödinger Hamiltonian (arrived at by numerical integration) was compared with the spectrum computed by the method of potential envelopes[2,3]. The use of (4.1) as a model for atomic interactions has a long history. As far back as 1935 Hellmann[53] employed $V(r)$ as a model for the interaction between the outer electron and the atomic core in alkali metals. Other

workers adopted this potential for similar applications[54]. More recently, it has been used to represent interactions for a variety of physical problems: - in the study of the thermodynamics of nonideal plasmas it was found that the properties of the interaction between an electron and an ion of the plasma can be described by a potential of the form (1.1)[55]; the two-particle interaction potential between the charged particles in polar crystals is also well approximated by such a potential[56]; Das and Chakravarty[57] have proposed that the CY potential be used in the form of a screened Coulomb potential in the study of inner-shell ionization problems.

We next discuss the features of this potential in more detail.

4.1 The Coulomb-plus-Yukawa potential

By making use of a simple transformation (scaling) one of the parameters in (4.1) can be eliminated[52]. Changing the scale of the radial variable $r \longrightarrow x = \lambda r$ and representing the eigenvalues of the Hamiltonian H by $E(\beta, \gamma, \lambda)$ we arrive at the following relation

$$E(\beta, \gamma, \lambda) = \lambda^2 E(\beta/\lambda, \gamma/\lambda, 1) \ , \quad \lambda > 0. \qquad (4.2)$$

As a result only the eigenvalues $E(\beta, \gamma, 1) = E(\beta, \gamma)$

corresponding to the Hamiltonian

$$H = -\Delta - \frac{\beta}{r} + \frac{\gamma}{r} e^{-r}, \qquad (4.3)$$

need concern us here.

Not only is (4.1) a linear combination of two well known potentials but it also has a simple shape. As can be seen from fig.4.1, for values of the parameter γ in the interval $\gamma < \beta$, the CY potential is attractive and Coulombic for small r. For $\gamma > \beta$, $V(r)$ no longer looks Coulombic but resembles a molecular potential of the Kratzer variety[58] (fig.4.2). We will restrict our attention to the case $\gamma < \beta$ since this makes the problem amenable to analysis by both of the approximation techniques of interest. To apply the method of potential envelopes in deducing the spectrum of (4.3), the theory of chapter 1 must be invoked; an outline of this procedure is presented in the next section.

4.2 Application of the method of potential envelopes to the Coulomb-plus-Yukawa potential

In chapter 1 it was shown that the theory of potential envelopes makes use of potentials for which the Schrodinger equation is exactly soluble to approximate the spectrum of problems which are immune to analytical methods. In the

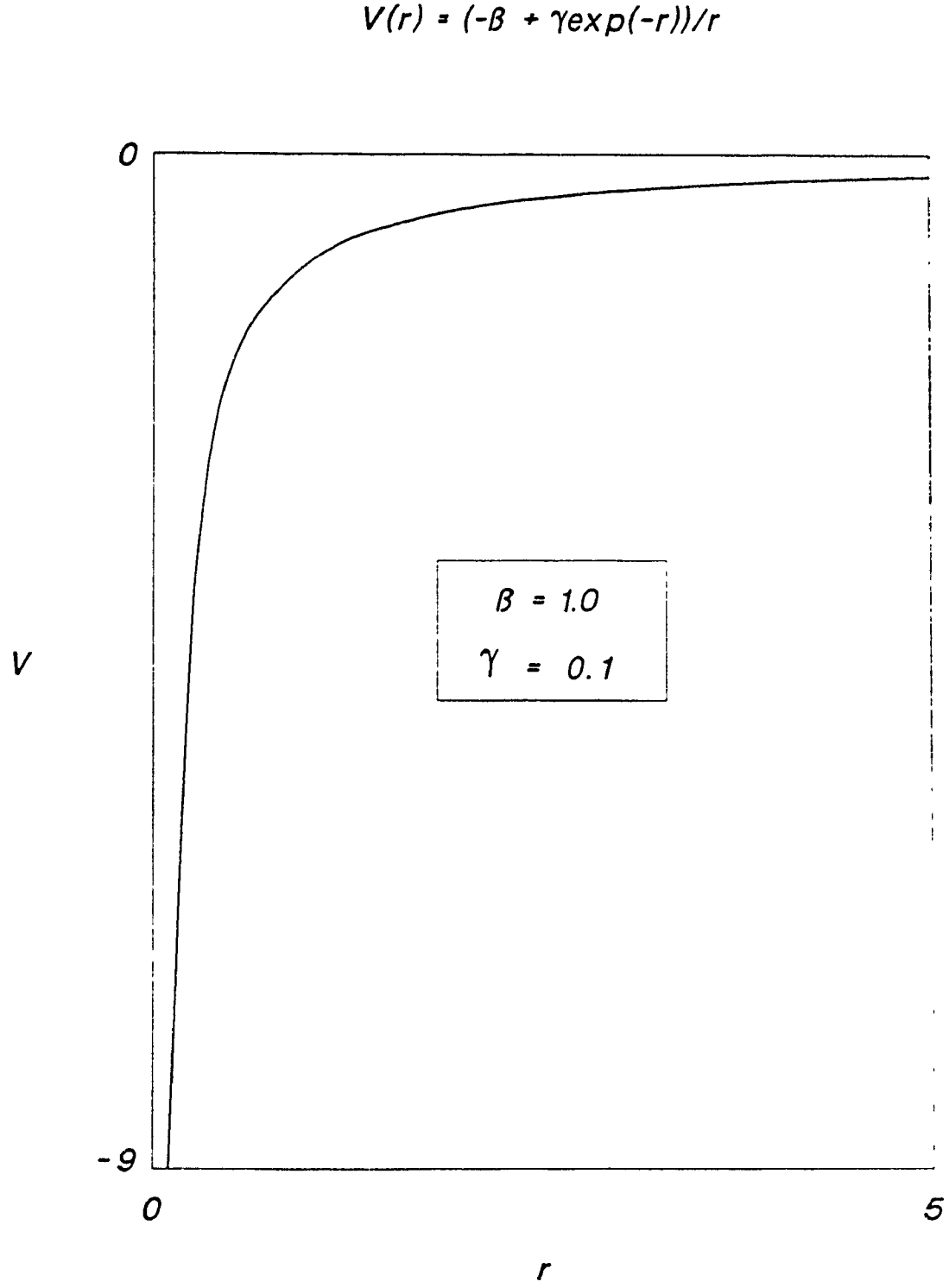

Fig.4.1 The CY potential for γ<ß

$$V(r) = (-\beta + \gamma exp(-r))/r$$

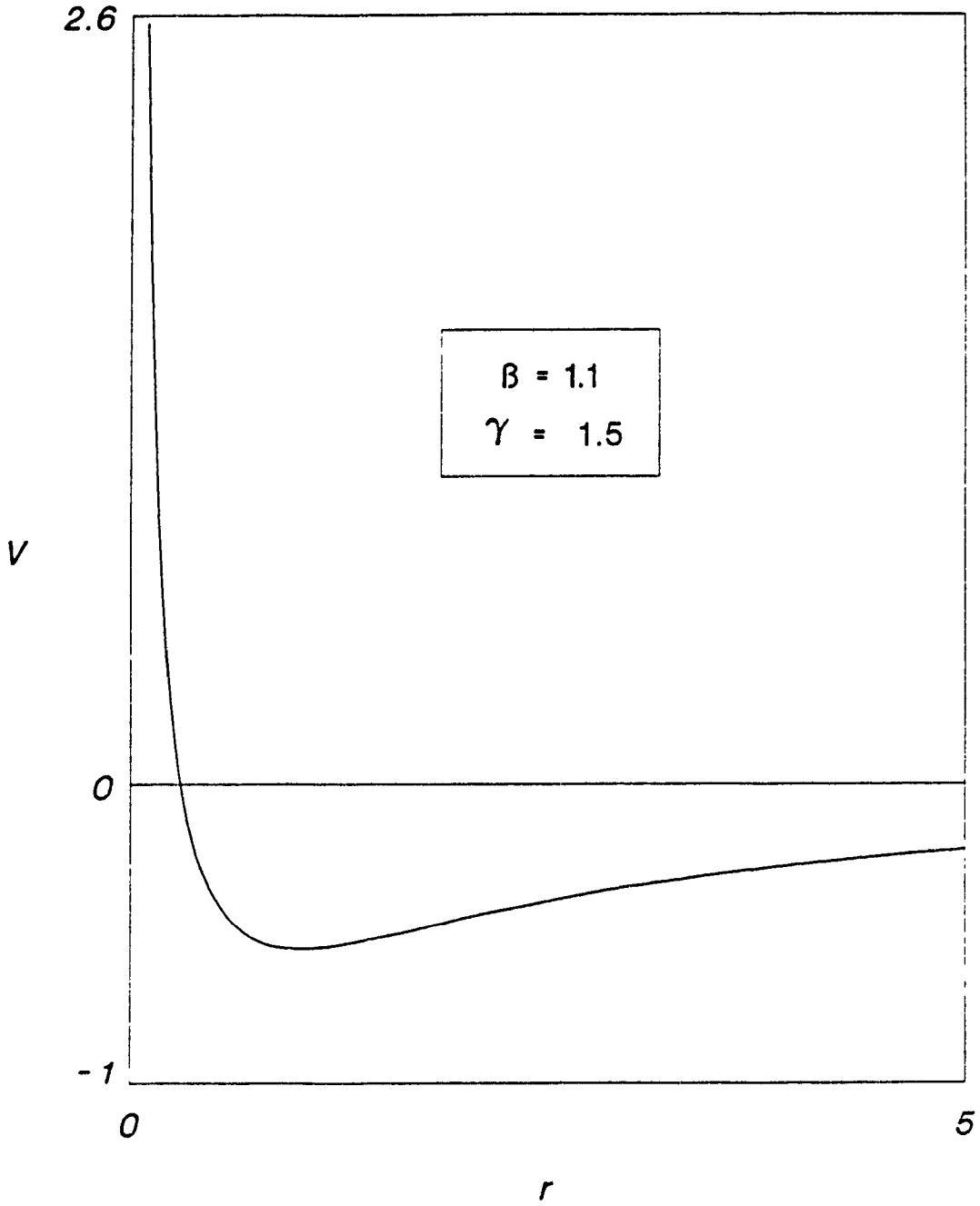

Fig.4.2 The CY potential for $\gamma > \beta$

case of potentials which can be expressed as smooth transformations of potentials for which an exact solution is available this is easily accomplished. All that is required is that the transformation have a definite *convexity*. For the CY potential an appropriate choice of basis potential is the Coulomb potential $h(r) = -1/r$. We consequently represent $V(r)$ as a smooth transformation of $h(r)$, that is

$$V(r) = g(-1/r). \tag{4.4}$$

For this choice of h and $\forall r > 0$ the transformation function g is *concave* for $\gamma < 0$, and *convex* for $0 < \gamma < \beta$. By (1.29) we know therefore that Coulomb envelopes result in either upper or lower bounds to the energies. Thus, we have

$$E_{n\ell} \approx \min_{r>0} \left\{ \frac{(n+\ell)^2}{r^2} - \frac{\beta}{r} + \frac{\gamma}{r} e^{-r} \right\}, \tag{4.5}$$

where $\approx = \geq$ if $0 < \gamma < \beta$ and $\approx = \leq$ if $\gamma < 0$.

Since this approximation is based on the Coulomb potential, it implies that the approximate spectrum inherits the degeneracies of the hydrogenic atom. Thus, even though the actual spectrum $\{E_{n\ell}\}$ does not share this Coulomb degeneracy, our *approximate* spectrum provides the same bound for each set of eigenvalues with $(n + \ell)$ = constant. It is the formula (4.5) that is central to the whole discussion. The simple minimization is quickly and easily carried out with the help of a computer. The results of these

computations, carried out on a micocomputer, will be presented in §4.4 along with the *JWKB* results.

We next formulate the *JWKB* approximation for the CY potential.

4.3 The *JWKB* approximation and the Coulomb-plus-Yukawa potential

The *JWKB* quantization condition in three-dimensions (3.47) can be readily applied to the CY potential. To simplify the calculation we will rescale (3.47) by the method set out in chapter 3 (§3.4) which for *S*-states becomes

$$\int_0^{r_c} \left[E - V(r)\right]^{1/2} dr = n\pi \ , \qquad n = 1,2,3,... \tag{4.6}$$

where $V(r)$ is given by (4.1) and $r_c = V^{-1}(E)$. For states with $\ell > 0$ the correct formula is

$$\int_{r_{min}}^{r_{max}} \left[E - V(r) - \frac{(\ell + 1/2)^2}{r^2}\right]^{1/2} dr = \left(n - \tfrac{1}{2}\right)\pi \ , \qquad n = 1,2,3,... \tag{4.7}$$

with r_{min}, and r_{max} defined by $V(r_{min}) = V(r_{max}) = E$. Once again the implementation of these recipes requires the use of a computer. The energies E are basically the zeros of

(4.6) and (4.7) and E appears both in the integrand and in the upper limit. This makes for a rather interesting problem in computer programming involving both minimization and inversion. To perform this calculation for any value of n or ℓ a program was written in the FORTRAN language (see Appendix A) and implemented on a microcomputer. The results for E as a function of the potential parameters β, γ and the quantum number n are presented in the next section.

4.4 Bound-state energies of the Coulomb-plus-Yukawa potential by potential envelopes and the *JWKB* approximation

To be able to compare the approximate eigenvalues with the exact ones another program was written which makes use of a finite-element method to integrate the Schrödinger equation numerically. The results of these calculations for a few eigenvalues of the spectrum are presented in Table 4.1 below. It is clear from these values that the energies derived by potential envelope theory, while good approximations, are not as close to the true energies as are those derived by the *JWKB* method. Nonetheless the method of potential envelopes provides a simple formula for *upper-bounds* to the eigenvalues. This formula, consisting basically of the minimization of a function, is also very simple to encode, for computational purposes. Moreover, it

is evident that in both cases the approximations improve in the classical limit $n \longrightarrow \infty$.

The special case $\beta = 0$, $\gamma = -2\alpha Z$, $\lambda = 1.13\alpha Z^{1/3}$ where $\alpha = (137.037)^{-1}$ is the fine-structure constant and Z the atomic number, reduces the CY potential to $V(r) = -2\alpha Z e^{-\lambda r}/r$[52]. This is the form taken by the Yukawa potential in atomic-physics applications and is appropriate for modeling the energy levels of neutral atoms. The method of potential envelopes has been applied to this potential by Richard Hall in an earlier paper[9]. We now clarify how the energies obtained from (4.5) are related to our results in *keV*. For Z = 1 and $\lambda = 0$, $V(r) \longrightarrow -2\alpha/r$, resulting in the hydrogenic spectrum,

$$E_{n\ell} = \frac{-\alpha^2}{(n+\ell)^2} \tag{4.8}$$

Thus, the conversion factor from $E_{n\ell}$ to energies in *kev* is given by the relation

$$\text{Energy} = (13.6047/1000\alpha^2)E_{n\ell}\ keV = 255.485\ E_{n\ell}\ keV. \tag{4.9}$$

Employing the shifted large-N approximation (see ch.2) Dutt *et al.*[59] also calculated the bound state energies. McEnnan *et.al.*[60] used perturbation theory to do the same. Hall's[9] bounds on $E_{n\ell}$ along with the results of Dutt *et.al.* and those of McEnnan *et.al.* are presented in

Table 4.2. Both Dutt *et.al.'s* and McEnnan *et.al.'s* results are of higher accuracy than those which we have found with the aid of potential envelopes, however the computational effort required is correspondingly much more.

4.5 Comparison of potential envelopes and a variational method

Adamowski[61] was the first to undertake a systematic investigation of the bound-state energies of the Coulomb-plus-Yukawa potential. Using a variational method, he obtained very accurate results for a wide range of potential parameters (β, γ, λ) and quantum numbers (n,ℓ). To compare our results with those of Adamowski we adopt his scale of units for the length (r) and energy. With $\beta = 2$, $\gamma < \beta$, and $\lambda > 0$, we have :

$$V(r) = -\frac{2}{r} + \frac{\gamma}{r} e^{-\lambda r}. \qquad (4.10)$$

Adamowski obtained very accurate results by using a ten-parameter trial wave function. In fact, to the precision quoted, his results are about as accurate as those obtained by integrating the Schrödinger equation numerically. Table 4.3 contrasts our results with those of Adamowski[52]. As is evident, potential envelopes give good results for a wide range of potential parameters. Though

the accuracy of Adamowski's results is in general superior to that of the potential envelope method, this is not always the case. For instance, for small values of the screening parameter λ of the Yukawa component, our results are just as accurate. This is due to the similarity in shape of the Coulomb-plus-Yukawa and the Coulomb potential (which we employ as our basis potential), for this range of λ.

Table 4.1 a),b),c) Eigenvalue upper bounds for the Schrödinger Hamiltonian $H = -\Delta - \beta/r + \gamma e^{-r}/r$ obtained by the method of potential envelopes (E_{PE}), along with the results of the *JWKB* approximation. The exact values (E_{NUM}) obtained by numerical integration are presented for comparison.

(a)

$\beta = 1,\ \gamma = -0.1$

n	ℓ	E_{PE}	E_{JWKB}	E_{NUM}
1	0	−0.25720	-0.26597	-0.26319
2	0	-0.06250	-0.06430	-0.06392
4	0	-0.01563	-0.01584	-0.01580
5	0	-0.01000	-0.01011	-0.01009
1	1	-0.06250	-0.06265	-0.06266
2	1	-0.02778	-0.02783	-0.02783
4	1	-0.01000	-0.01001	-0.01001
5	1	-0.00694	-0.00695	-0.00695

(b)

$\beta = 1,\ \gamma = -0.5$

n	ℓ	E_{PE}	E_{JWKB}	E_{NUM}
1	0	−0.29752	-0.34357	-0.33219
2	0	-0.06252	-0.07173	-0.07031
4	0	-0.01563	-0.01670	-0.01653
5	0	-0.01000	-0.01054	-0.01009
1	1	-0.06252	-0.06331	-0.06333
2	1	-0.02778	-0.02806	-0.02805
4	1	-0.01000	-0.01006	-0.01006
5	1	-0.00694	-0.00698	-0.00698

(c)

$\beta = 1,\ \gamma = -1.0$

n	ℓ	E_{PE}	E_{JWKB}	E_{NUM}
1	0	−0.38989	-0.48447	-0.46726
2	0	-0.06254	-0.08172	-0.07952
4	0	-0.01563	-0.01775	-0.01751
5	0	-0.01000	-0.01106	-0.01095
1	1	-0.06254	-0.06431	-0.06430
2	1	-0.02778	-0.02839	-0.02836
4	1	-0.01000	-0.01014	-0.01013
5	1	-0.00694	-0.00703	-0.00702

Table 4.2 Bound-state eigenvalue upper bounds for the Yukawa potential $V(r) = -2\alpha Z e^{-\lambda r}/r$ in *keV* (neutral atoms), along with the results of the shifted $1/N$ approximation of Dutt *et. al*[59], and those of McEnnan *et. al.*[60] (labelled 'Analytic perturbation'); numerical results are presented for comparison. The Yukawa potential corresponds to the case $\beta = 0$ for the Coulomb - plus - Yukawa potential.

Z	n	ℓ	Envelope	Shifted $1/N$	Analytic perturbation	Numerical
13	1	0	-1.450	-1.488	-1.484	-1.488
36	1	0	-14.16	-14.24	-14.24	-14.24
	2	0	-1.437	-1.676	-1.615	-1.692
	1	1	-1.437			-1.566
79	1	0	-74.80	-74.91	-74.95	-74.95
	2	0	-12.00	-12.49	-12.45	-12.50
	1	1	-12.00			-12.25

Tables 4.3(a) and 4.3(b) Some eigenvalue upper bounds for the Coulomb - plus - Yukawa potential as functions of λ, for $\gamma = -1$ and $\gamma = -10$, obtained with Eq. (1.29). For comparison, the variational results from Ref. (61) are given in parentheses.

(a)

$\gamma = -1$

λ =	0.01	0.05	0.1	0.2	0.5	1.0
n ℓ						
1 0	-2.24003	-2.20082	-2.15326	-2.06278	-1.82531	-1.52578
	(-2.24005)	(-2.20122)	(-2.15479)	(-2.06840)	(-1.85302)	(-1.60149)
2 0	-0.55263	-0.51569	-0.47478	-0.40816	-0.29752	-0.25520
	(-0.55270)	(-0.51714)	(-0.47984)	(-0.42373)	(-0.34092)	(-0.30213)
3 0	-0.13114	-0.10204	-0.08066	-0.06563	-0.06252	-0.06250
	(-0.13138)	(-0.10602)	(-0.09015)	(-0.07869)	(-0.07139)	(-0.06830)
1 1	-0.55263	-0.51569	-0.47478	-0.40816	-0.29752	-0.25520
	(-0.55270)	(-0.51714)	(-0.47984)	(-0.42373)	(-0.34092)	(-0.30213)
2 1	-0.24029	-0.20684	-0.17525	-0.13728	-0.11246	-0.11113
	(-0.24040)	(-0.20900)	(-0.18172)	(-0.15144)	(-0.12596)	(-0.11635)

(b)

$\gamma = -10$

n ℓ	λ = 0.01	0.05	0.1	0.2	0.5	0.85
1 0	-35.9001	-35.5021	-35.0083	-34.0330	-31.2030	-28.0768
	(-35.9001)	(-35.5031)	(-35.0124)	(-34.0489)	(-31.2967)	(-28.3300)
2 0	-8.9003	-8.5082	-8.0326	-7.1281	-4.7613	-2 6037
	(-8.9005)	(-8.5122)	(-8.0482)	(-7.1862)	(-5.0617)	(-3 2972)
3 0	-2.1513	-1.7820	-1.3737	-0.7185	-0.0627	-0 0625
	(-2.1520)	(-1 7966)	(-1.4254)	(-0.8800)	(-0.2431)	(-0 1503)
1 1	-3.9003	-8.5082	-8.0300	-7.1280	-4.7613	-2.6037
	(-8.9004)	(-8.5102)	(-8.0404)	(-7.1569)	(-4.9105)	(-2.9522)
2 1	-3.9007	-3.5183	-3.0717	-2.2761	-0.5952	-0.1117
	(-3 9010)	(-3.5251)	(-3.0968)	(-2.3638)	(-0.9507)	(-0.3367)

CONCLUSION

The discrete part of the spectrum of the Schrödinger operator $H = K + V$ may be characterised as the set of minima of the Rayleigh quotient $(\psi,H\psi)/(\psi,\psi)$. The eigenfunctions ψ_i of H which solve this minimization problem optimize the trade-off between the kinetic and potential energies. The potential envelope formalism recasts this optimization problem into the semi-classical form:

$$E_{n\ell} \approx \min_{r>0} \left\{ K_{n\ell}(r) + V(r) \right\}, \qquad (1)$$

where $K_{n\ell}(r)$ represents the mean kinetic energy and V is a smooth transformation $V(r) = g(h(r))$ of a soluble potential h. If the transformation g possesses a definite convexity then the formula (1) provides bounds to the energies.

The large-N approximation was reviewed and then conveniently analysed in terms of the envelope method. It was demonstrated that the latter technique provides tighter bounds to the energies than does the large-N approximation[1].

One of the oldest and most interesting semi-classical methods, the *JWKB* approximation, furnishes approximations to the eigenvalues which are often very good. These approximations are provided by an expression in integral form. This is in contrast to the potential envelope method

and the large-*N* approximation both of whose approximation formulas involve differentiation. The problem of determining what bounds (if any) *JWKB* approximate energies provide to the true energies is a particularly interesting and challenging one. It was discovered that the *JWKB* approximate eigenvalues can be employed to establish loose upper and lower bounds to the exact energies[48]. Meanwhile, the method does not immediately yield to an analysis via the potential envelope method, as does the large-*N* approximation.

The bound-state spectrum of a particle moving under the influence of the Coulomb-plus-Yukawa potential was explored. This was done with the aid of both the *JWKB* approximation and the method of potential envelopes. Although the implementation of the *JWKB* approximation can be difficult, this limitation becomes less significant as the power of computers increases.

The question of *JWKB* error bounds is fascinating. Eventually we may have at our disposal an analysis of *JWKB* which will include error estimates, and therefore could sharpen this important tool for elucidating the relation between a potential and the spectrum it generates.

APPENDIX A

COMPUTER PROGRAM

The nature of the *JWKB* eigenvalue approximation formulae is such that in general a computer greatly simplifies the problem of computation.

To evaluate the eigenenergies of the Coulomb-plus-Yukawa potential a program was written in FORTRAN. The algorithm basically consists of finding the zeros of the *JWKB* function (*the JWKB* quantization condition) in a single dimension. This function is expressed in integral form which implies that within the context of the general zero-finder a numerical integration must be performed. An interesting feature of the problem is the presence of the energies $E_{n\ell}$ both in the integrand and in the *limits* of integration. This makes for a much more challenging situation. The energies appearing in the limits must first be numerically inverted in order that the radial variable (the variable of integration) be made explicit.

The different subroutines required for the implementation of this program were derived from a popular text on applied numerical methods[62].

LIST OF ORIGINAL SUBROUTINES

FUNC

FWKB

POT

FNC

Other subroutines are either direct or modified versions of subroutines from *NUMERICAL RECIPES*[62].

```
*****************************************************************
*                                                               *
*                        PROGRAM: JWKB-C+Y                      *
*                                                               *
*   This program calculates the Eigenvalues of the Coulomb-plus-Yukawa  *
*   potential by the JWKB quantization condition, it requires FUNC as   *
*   well as FWKB, FNC and POT; FUNC defines the "JWKB" function for which *
*   the zero is to be found, FWKB defines the JWKB integrand, FNC is used *
*   to find the lower and upper limits of the integral (must find the   *
*   zero(es) of the integrand), POT defines the potential.              *
*                                                               *
*****************************************************************


*   USES: FWKB, POT, FNC, FUNC, QROMB2, POLINT, TRAPZD2, ZBRENT2, ZBRENT3,
*         MNBRAK, GOLDEN.


      REAL E, L, N, EMIN, EMAX, TOL, STOEIG(100)
      INTEGER NN, NCOUNT
      CHARACTER*1 C1, FIL, STARTC

      PARAMETER(TOL=1.0E-7)
      EXTERNAL FUNC,ZBRENT2
      COMMON STOEIG


*   define the bounds for the the energy E, ZBRENT2 uses these to
*   find the zero of FUNC which defines the JWKB quantization condition.

5     PRINT*,'ENTER QUANTUM # N'
      READ*,N

      PRINT*,'ENTER QUANTUM # L'
      READ*,L
      IF( L .EQ. 0.0) THEN
          EMIN=-0.40
          EMAX=-1.0E-3
C         EMIN=-5.80
C         EMAX=-1.0E-8
      ELSE
          EMIN=-0.10
          EMAX=-0.0025
      ENDIF

*       Print eigenvalue.

      E = ZBRENT2(FUNC,EMIN,EMAX,N,L,TOL)
```

```
      PRINT*,' '
      PRINT*,'DESIRED EIGENVALUE IS',E
      PRINT*,' '
60    PRINT*,' '
      PRINT*,'ONE MORE TIME ?'
      READ 20,C1
      PRINT*,C1

      IF(C1.EQ.'N') THEN
          GOTO 35
      ELSE
          GOTO 5
      ENDIF

10    FORMAT(' ',30X,I1,')',3X,A10)
20    FORMAT(A1)
40    FORMAT(I3,I3)
45    FORMAT(F10.6)
50    FORMAT(A4)

35    END

*     Defines the JWKB function to be minimized (LHS-RHS of quantization
*     relation).

      FUNCTION FUNC(E,N,L)
      REAL L, N, RMIN, RMAX, POTMIN, PI
      EXTERNAL FWKB, FNC, POT
      PARAMETER(TOL=1.0E-6)

      PI=3.141592654

*     Establish the bounds for the root search for the limits of WKB integral.

      RMIN = 1.0E-15
      RMID = 1.0E2
      RMAX = 1.0E15

*     Find root(s) for limit(s). If L = 0 then only one zero exists.
*     If L > 0 then MNBRAK brackets and GOLDEN finds the minimum of
*     the potential so that it is a simple matter to locate the two
*     limits which are simply the roots of the JWKB integrand. ZBRENT3
*     finds the root(s).

*     A and B are the limits for the JWKB integral.

*     NOTE: we cannot use ZBRENT2 since it has already been opened
*     in the call from the main program, therefore we make a copy
*     of ZBRENT2 and label it ZBRENT3 which we employ below.

      IF ( L .EQ. 0.0 ) THEN
          A = 0.0
          B = ZBRENT3(FNC,RMIN,RMAX,E,L,TOL)
```

```
      ELSE
          CALL MNBRAK(RMIN,RMID,CX,FA,FB,FC,L,POT)
          FMIN = GOLDEN(RMIN,RMID,CX,L,POT,TOL,POTMIN)
          A = ZBRENT3(FNC,RMIN,POTMIN,E,L,TOL)
          B = ZBRENT3(FNC,POTMIN,RMAX,E,L,TOL)
      ENDIF


*     Evaluate JWKB integral.

      CALL QROMB2(FWKB,A,B,E,L,S)

*     Define the function (FUNC) to be minimized.

      IF ( L .EQ. 0.0 ) THEN
          FUNC = 2.0*S - PI*N
      ELSE
          FUNC = S - PI*( N - 0.5 )
      ENDIF
      END


*     This function defines the JWKB integrand to be used with QSIMP
*     and other integration routines.

      REAL FUNCTION FWKB(E,L,r)
      REAL E, L, r
      EXTERNAL POT
      IF( L .EQ. 0.0 ) THEN
          FWKB = SQRT(ABS(E*r*r - POT(r,L)))
      ELSE
          FWKB = SQRT(ABS(E - POT(r,L)))
      ENDIF
      END


*     This function defines a pot'l for use with JWKB functions.

      REAL FUNCTION POT(r,L)
      REAL L, r
      B = 1.0
      G = 0.1
      IF ( L .EQ. 0.0 ) THEN
          POT = -B - G*EXP(-r*r) + L*(L + 1.0)
      ELSE
          POT = (-B/r) - (G*EXP(-r)/r) + ((L + 0.5)**2)/(r*r)
      ENDIF
      END


*     FNC defines the part of the JWKB integrand within the square-root,
*     it is used to find the limits for the JWKB integral (LHS of the
*     quantization condition) using ZBRENT3.
```

```
      FUNCTION FNC(r,E,L)
      REAL r, E, L
      B = 1.0
      G = 0.1
      IF ( L .EQ. 0.0 ) THEN
          FNC = E*r*r + B + G*EXP(-r*r) - L*(L + 1.0)
      ELSE
          FNC = E + (B/r) + (G*EXP(-r)/r) - ((L + 0.5)**2)/(r*r)
      ENDIF
      END


      SUBROUTINE QROMB2(FUNC,A,B,E,L,SS)

*     This is amodified version of QROMB.
*     Returns as S the integral of the function FUNC from A to B.
*     Integration is performed by Romberg's method of order 2K, where
*     e.g., K=2 is Simpsons rule.

      PARAMETER(EPS=1.0E-7, JMAX=20, JMAXP=JMAX+1, K=5, KM=K-1)

*     Here EPS is the fractional accuracy desired, as determined by the
*     extrapolation error estimate; JMAX limits the total number of steps;
*     K is the number of points used in the extrapolation.

*     These store the successive trapezoidal approximations and their
*     relative step-sizes.

      DIMENSION S(JMAXP), H(JMAXP)
      REAL E, L
      EXTERNAL FUNC
      H(1)=1.0
      DO J=1, JMAX
          CALL TRAPZD2(FUNC,A,B,E,L,S(J),J)
          IF(J .GE. K) THEN
              CALL POLINT(H(J-KM),S(J-KM),K,0.0,SS,DSS)
              IF(ABS(DSS) .LT. EPS*ABS(SS)) RETURN
          ENDIF
          S(J+1)=S(J)

*     This is a key step: The factor is 0.25 even though the step-size
*     is decreased by only 0.5. This makes the extrapolation a polynomial
*     in h*h as allowed by equation (4.2.1), not just a polynomial in h.

          H(J+1)=0.25*H(J)
      ENDDO
      PAUSE 'TOO MANY STEPS'
      END
```

```
      SUBROUTINE TRAPZD2(FUNC,A,B,E,L,S,N)

*     This is altered version if TRAPZD (NUMERICAL RECIPES).
*     This routine computes the Nth stage of refinement of an extended
*     trapezoidal rule. FUNC is input as the name of the function to be
*     integrated between limits A and B, also input. When called with N=1
*     the routine returns as S the crudest estimate of INT(f(x)).
*     Subsequent calls with N=2,3,... (in that sequential order) will
*     improve the accuracy of S by adding 2^(N-2) additional interior
*     points. S should not be modified between sequential calls.

      REAL E,L
      IF (N.EQ.1) THEN
          S=0.5*(B-A)*(FUNC(E,L,A)+FUNC(E,L,B))
          IT=1
      ELSE
          TNM=IT
          DEL=(B-A)/TNM
          X=A+0.5*DEL
          SUM=0.
          DO 11 J=1,IT
              SUM=SUM+FUNC(E,L,X)
              X=X+DEL
11        CONTINUE
          S=0.5*(S+(B-A)*SUM/TNM)
          IT=2*IT
      ENDIF
      RETURN
      END


      SUBROUTINE POLINT(XA,YA,N,X,Y,DY)

*     Given arrays XA and YA, each of length N, and given a value X,
*     this routine returns a value of Y, and an error estimate DY.
*     If P(x) is the polynomial of degree N-1 such that  P(XAi)=YAi,
*     i=1,...,N, then the returned value Y=P(x).

*     Change NMAX as desired to be the largest anticipated value of N.

      PARAMETER(NMAX=10)
      DIMENSION XA(N), YA(N), C(NMAX), D(NMAX)
      NS=1
      DIF=ABS(X-XA(1))

*     Here we find the index NS of the closest table entry,

      DO I=1,N
          DIFT=ABS(X-XA(I))
          IF(DIFT. LT. DIF) THEN
              NS=I
              DIF=DIFT
          ENDIF
```

```
*   and initialize the tableau of C's and D's.

          C(I)=YA(I)
          D(I)=YA(I)
      ENDDO

*   This is the initial approximation to Y.

      Y=YA(NS)
      NS=NS-1
*   For each column of the tableau we loop over the current C's and D's
*   and update them.

      DO M=1, N-1
          DO I=1, N-M
              HO=XA(I)-X
              HP=XA(I+M)-X
              W=C(I+1)-D(I)
              DEN=HO-HP

*   This error can occur only if two input XA's are (to within roundoff)
*   identical.

              IF(DEN .EQ. 0.0) PAUSE
              DEN=W/DEN

*   Here's the C's and D's are updated.

              D(I)=HP*DEN
              C(I)=HO*DEN
          ENDDO

*   After each column in the tableau is completed, we decide which
*   correction, C or D, we want to add to our accumulating value of Y,
*   i.e. which path to take through the tableau - forking up or down.
*   We do this in such a way as to take the most "straight line" route
*   throught the tableau to its apex, updating NS accordingly to keep
*   track of where we are. This route keeps the partial approximations
*   centered (insofar as possible) on the target X. The last DY added
*   is thus the error indication.

          IF(2*NS .LT. N-M) THEN
              DY=C(NS+1)
          ELSE
              DY=D(NS)
              NS=NS-1
          ENDIF
          Y=Y+DY
      ENDDO
      RETURN
      END
```

```
      FUNCTION ZBRENT2(FUNC,X1,X2,N,L,TOL)

*     This is an altered version of ZBRENT (NUMERICAL RECIPES).
*     Using Brent's method, find the root of a function FUNC kno'  to lie
*     between X1 and X2. The root, returned as ZBRENT2, will be r fined
*     until its accuracy is TOL.

      REAL N, L
      PARAMETER(ITMAX=100, EPS=3.0E-8)
      A=X1
      B=X2
      FA=FUNC(A,N,L)
      FB=FUNC(B,N,L)
      IF (FB*FA.GT.0) PAUSE 'ROOT MUST BE BRACKETED FOR ZBRENT2'
      FC=FB
      DO 11 ITER=1,ITMAX
          IF (FB*FC.GT.0.) THEN
              C=A
              FC=FA
              D=B-A
              E=D
          ENDIF
          IF (ABS(FC).LT.ABS(FB)) THEN
              A=B
              B=C
              C=A
              FA=FB
              FB=FC
              FC=FA
          ENDIF
          TOL1=2.*EPS*ABS(B)+0.5*TOL
          XM=0.5*(C-B)
          IF(ABS(XM).LE.TOL1.OR.FB.EQ.0.) THEN
              ZBRENT2=B
              RETURN
          ENDIF
          IF (ABS(E).GE.TOL1 .AND. ABS(FA).GT.ABS(FB)) THEN
              S=FB/FA
              IF (A.EQ.C) THEN
                  P=2.*XM*S
                  Q=1.-S
              ELSE
                  Q=FA/FC
                  R=FB/FC
                  P=S*(2.*XM*Q*(Q-R)-(B-A)*(R-1.))
                  Q=(Q-1.)*(R-1.)*(S-1.)
              ENDIF
              IF (P.GT.0.) Q=-Q
              P=ABS(P)
              IF (2*P .LT. MIN(3.*XM*Q-ABS(TOL1*Q),ABS(E+Q))) THEN
                  E=D
                  D=P/Q
              ELSE
```

```
                D=XM
                E=D
            ENDIF
        ELSE
            D=XM
            E=D
        ENDIF
        A=B
        FA=FB
        IF (ABS(D) .GT. TOL1) THEN
            B=B+D
        ELSE
            B=B+SIGN(TOL1,XM)
        ENDIF
        FB=FUNC(B,N,L)
11    CONTINUE
      PAUSE 'ZBRENT2 EXCEEDING MAXIMUM # OF ITERATIONS.'
      ZBRENT2=B
      RETURN
      END


      FUNCTION ZBRENT3(FUNC,X1,X2,EE,L,TOL)

*     This is an altered version of ZBRENT (NUMERICAL RECIPES).
*     Using Brent's method, find the root of a function FUNC known to lie
*     between X1 and X2. The root, returned as ZBRENT2, will be refined
*     until its accuracy is TOL. We are including this copy of ZBRENT2 due
*     to conflicts inherent to FORTRAN (see FUNC above).

      REAL EE, L
      PARAMETER(ITMAX=100, EPS=3.0E-8)
      A=X1
      B=X2
      FA=FUNC(A,EE,L)
      FB=FUNC(B,EE,L)
      IF (FB*FA.GT.0) PAUSE 'ROOT MUST BE BRACKETED FOR ZBRENT3'
      FC=FB
      DO 11 ITER=1,ITMAX
        IF (FB*FC.GT.0.) THEN
            C=A
            FC=FA
            D=B-A
            E=D
        ENDIF
        IF (ABS(FC).LT.ABS(FB)) THEN
            A=B
            B=C
            C=A
            FA=FB
            FB=FC
            FC=FA
        ENDIF
```

```
      TOL1=2.*EPS*ABS(B)+0.5*TOL
      XM=0.5*(C-B)
      IF(ABS(XM).LE.TOL1.OR.FB.EQ.0.) THEN
        ZBRENT3=B
        RETURN
      ENDIF
      IF (ABS(E).GE.TOL1 .AND. ABS(FA).GT.ABS(FB)) THEN
        S=FB/FA
        IF (A.EQ.C) THEN
          P=2.*XM*S
          Q=1.-S
        ELSE
          Q=FA/FC
          R=FB/FC
          P=S*(2.*XM*Q*(Q-R)-(B-A)*(R-1.))
          Q=(Q-1.)*(R-1.)*(S-1.)
        ENDIF
        IF (P.GT.0.) Q=-Q
        P=ABS(P)
        IF (2*P .LT. MIN(3.*XM*Q-ABS(TOL1*Q),ABS(E+Q))) THEN
          E=D
          D=P/Q
        ELSE
          D=XM
          E=D
        ENDIF
      ELSE
        D=XM
        E=D
      ENDIF
      A=B
      FA=FB
      IF (ABS(D) .GT. TOL1) THEN
        B=B+D
      ELSE
        B=B+SIGN(TOL1,XM)
      ENDIF
      FB=FUNC(B,EE,L)
11    CONTINUE
      PAUSE 'ZBRENT3 EXCEEDING MAXIMUM # OF ITERATIONS.'
      ZBRENT3=B
      RETURN
      END


      SUBROUTINE MNBRAK(AX,BX,CX,FA,FB,FC,L,FUNC)

*  Given a function FUNC, and given distinct initial points AX and BX,
*  this routine searches in the downhill direction (defined by the
*  function as evaluated at the initial points) and returns new points
*  AX, BX, CX which bracket a minimum of the function. Also returned
*  are the function values at the three points FA, FB, and FC.
```

```
      REAL L
      PARAMETER(GOLD=1.618034, GLIMIT=100., TINY=1.0E-20)
*     The first parameter is the default ratio by which successive
*     intervals are magnified; the second is the maximium magnification
*     allowed for a parabolic-fit step.
      FA=FUNC(AX,L)
      FB=FUNC(BX,L)
*     Switch roles of A and B so that we can go downhill in the direction
*     from A to B.
      IF(FB.GT.FA) THEN
          DUM=AX
          AX=BX
          BX=DUM
          DUM=FB
          FB=FA
          FA=DUM
      ENDIF
*     First guess for C.
      CX=BX+GOLD*(BX-AX)
      FC=FUNC(CX,L)
*     "DO WHILE": keep returning here until we bracket.
1     IF(FB.GE.FC) THEN
          R=(BX-AX)*(FB-FC)
          Q=(BX-CX)*(FB-FA)
*     Compute U by parabolic extrapolation from A, B, C. TINY is used
*     to prevent any possible division by zero.
          U=BX-((BX-CX)*Q-(BX-AX)*R)/(2.0*SIGN(MAX(ABS(Q-R),TINY),Q-R))
*     We won't go farther than this.
          ULIM=BX+GLIMIT*(CX-BX)
*     Now to test various possibilities:
          IF((BX-U)*(U-CX).GT.0.0) THEN
*     Parabolic U is between B and C: try it.
              FU=FUNC(U,L)
*     Got a minimum between B and C.
              IF(FU.LT.FC) THEN
```

```
                AX=BX
                FA=FB
                BX=U
                FB=FU
```

- Which will exit

```
                GOTO 1
```

- Got a minimum between A and U.

```
            ELSEIF(FU.GT.FB) THEN
                CX=U
                FC=FU
```

- Got a minimum between A and U.

```
                GOTO 1
            ENDIF
```

- Parabolic fit was no use. Use default magnification.

```
            U=CX+GOLD*(CX-BX)
            FU=FUNC(U,L)
```

- Parabolic fit is between C and its allowed limit.

```
        ELSEIF((CX-U)*(U-ULIM).GT.0.0) THEN
            FU=FUNC(U,L)
            IF(FU.LT.FC) THEN
                BX=CX
                CX=U
                U=CX+GOLD*(CX-BX)
                FB=FC
                FC=FU
                FU=FUNC(U,L)
            ENDIF
```

- Limit parabolic U to maximum allowed value.

```
        ELSEIF((U-ULIM)*(ULIM-CX).GE.0.0) THEN
            U=ULIM
            FU=FUNC(U,L)
        ELSE
```

- Reject parabolic U, use dfault magnification.

```
            U=CX+GOLD*(CX-BX)
            FU=FUNC(U,L)
        ENDIF
```

- Eliminate oldest point and continue.

```
        AX=BX
        BX=CX
        CX=U
        FA=FB
        FB=FC
        FC=FU
        GOTO 1
      ENDIF
      RETURN
      END


      FUNCTION GOLDEN(AX,BX,CX,L,F,TOL,XMIN)

*     Given a function F and given a bracketing triplet of abcissas AX,
*     BX, CX (such that BX is between AX and CX, and F(BX) is less than
*     both F(AX) and F(CX)), this routine performs a golden section
*     search for the minimum, isolating it to a fractional precision of
*     about TOL. The abscissa of the minimum is returned as XMIN, and
*     the minimum function value is returned as GOLDEN, the returned
*     function value.
*      Golden ratios

        REAL L
        PARAMETER(R=0.61803399, C=1.0-R)

*     At any given time we will kep track of four points, X0,X1,X2,X3.

        X0=AX
        X3=CX

*     Make X0 to X1 the smaller segment,

        IF(ABS(CX-BX).GT.ABS(BX-AX)) THEN
            X1=BX

*     and fill in the new point to be tried.

            X2=BX+C*(CX-BX)
        ELSE
            X2=BX
            X1=BX-C*(BX-AX)
        ENDIF

*     The initial function evaluations. Note that we never need to
*     evaluate the function at the original endpoints.

        F1=F(X1,L)
        F2=F(X2,L)

*     DO-WHILE loop; we keep returning here.

1       IF(ABS(X3-X0).GT.TOL*(ABS(X1)+ABS(X2))) THEN
```

- One possible outcome,

```
IF(F2.LT.F1) THEN
```

- Its housekeeping,

```
X0=X1
X1=X2
X2=R*X1+C*X3
F0=F1
F1=F2
```

- and a new function evaluation.

```
F2=F(X2,L)
```

- The other outcome,

```
ELSE
    X3=X2
    X2=X1
    X1=R*X2+C*X0
    F3=F2
    F2=F1
```

- and its new function evaluation.

```
    F1=F(X1,L)
ENDIF
```

- Back to see if we are done.

```
GOTO 1
ENDIF
```

- We are done. Output the best of the two current values.

```
IF(F1.LT.F2) THEN
    GOLDEN=F1
    XMIN=X1
ELSE
    GOLDEN=F2
    XMIN=X2
ENDIF
RETURN
END
```

APPENDIX B

Spectrum of the Coulomb-plus-Yukawa potential by the method of potential envelopes

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Received September 9, 1991

The method of potential envelopes is used to analyse the bound-state spectrum of the Schrödinger Hamiltonian $H = -\Delta + V(r)$, where $V(r) = -\beta/r + \gamma e^{-\lambda r}/r$, $\gamma < \beta$. It is established that upper or lower bounds to the eigenenergies $E_n(\beta,\gamma,\lambda)$ are generated by the simple formula, $E_n \approx \min_{l\geq 0}\{(n+l)^2/r^2 + V(r)\}$, where $\approx = \leqslant$ if $\gamma < 0$ and $\approx = \geqslant$ if $\gamma > 0$. The results are compared with eigenvalues computed numerically by a finite-element method and also with the results of a variational calculation.

La methode des enveloppes de potentiel est utilisee pour analyser le spectre des etats lies de l'hamiltonien de Schrodinger $H = -\Delta + V(r)$, ou $V(r) = -\beta/r + \gamma e^{-\lambda r}/r$, $\gamma < \beta$. Il est montre que les limites superieure et inferieure des energies proposees $E_n(\beta,\gamma,\lambda)$ sont obtenues par la formule simple $E_n \approx \min_{l\geq 0}\{(n+l)^2/r^2 + V(r)\}$, ou $\approx = \leqslant$ si $\gamma < 0$ et $\approx = \geqslant$ si $\gamma > 0$. On compare les resultats avec les valeurs propres calculées numeriquement par une methode aux elements finis et également avec les resultats d'un calcul par la methode des variations.

[Traduit par la redaction]

Can. J. Phys. 69, 1362 (1991)

1. Introduction

The purpose of this article is to use the method of potential envelopes (1, 2) to derive a simple approximate formula for the bound-state spectrum of a single particle moving in the Coulomb-plus-Yukawa potential

$$[1.1]\quad V(r) = -\frac{\beta}{r} + \frac{\gamma}{r}e^{-\lambda r}$$

$$\beta > 0, \qquad \gamma < \beta, \qquad \lambda > 0$$

This central potential was first proposed by Hellmann (3) in 1935 to model the interaction between the valence electron and the atomic core in alkali metals. Other workers adopted this potential for similar applications (4). More recently, it has been used to represent interactions for a variety of physical problems. In the study of the thermodynamics of nonideal plasmas, it was found that the properties of the interaction between an electron and an ion of the plasma can be described by a potential of the form [1.1] (5); the two-particle interaction potential between the charged particles in polar crystals is also well approximated by such a potential (6). Das and Chakravarty (7) proposed that the Coulomb-plus-Yukawa potential be used in the form of a screened Coulomb potential in the study of inner-shell ionization problems.

The spectrum that concerns us is that of the Schrodinger Hamiltonian H

$$[1.2]\quad H = -\Delta + V(r)$$

This eigenvalue problem has been studied by other workers, using various techniques. Adamowski (8) was the first to undertake a systematic investigation of the bound-state energies. Using a 10-parameter variational method, he obtained very accurate results for a wide range of potential parameters (β,γ,λ) and quantum numbers n. Dutt *et al.* (9) employed the shifted large-V approximation and produced good results for small values of the screening parameter λ, and weak coupling of the Yukawa component (small γ). More recently, Bag *et al.* (10) utilized Rayleigh–Schrodinger perturbation theory and derived an analytic expression for the bound-state energies. While the method of potential envelopes is not in general capable of achieving accuracies of the order of those of Adamowski (8), it provides a simple formula for *bounds* to the eigenvalues.

The problem at hand can be simplified somewhat through the use of elementary scaling arguments. By representing the eigenvalues of H by $E(\beta,\gamma,\lambda)$ and changing the scale of the radial variable $r \rightarrow x = \lambda r$ we arrive at the following relation

$$[1.3]\quad E(\beta,\gamma,\lambda) = \lambda^2 E\left(\frac{\beta}{\lambda}, \frac{\gamma}{\lambda}, 1\right), \qquad \lambda > 0$$

This implies that only the eigenvalues $E(\beta,\gamma,1)$ corresponding to the Hamiltonian

$$[1.4]\quad H = -\Delta - \frac{\beta}{r} + \frac{\gamma}{r}e^{-r}$$

need be considered. In Sect. 4 we will adopt another scaling scheme to compare our results with those of Adamowski.

We will next motivate the main formula [1.6] from which all our results follow. (Sect. 2 of this paper consists of a short self-contained description of the method of potential envelopes.)

The backbone of envelope theory is its exploitation of exact solutions of the Schrodinger equation to approximate solutions of intractable problems. With this in mind, we express the potential $V(r)$ as a smooth transformation of the Coulomb potential, this latter potential, of course, is exactly soluble and will be the potential on which we base our approximations. We write $V(r) = g(-1/r)$ where $g(X)$ satisfies $g'(X) < 0$ for $X < 0$, $\gamma < 0$ or $g'(X) > 0$ for $X < 0$, $\gamma > 0$. $V(r)$ is then the envelope of a family $\{V_l(r)\}$ of tangential Coulomb potentials each of which has the form

$$[1.5] \quad V^{(n)}(r) = A(t) - vh(r) \left(\frac{-1}{r} \right) \approx V(r)$$

where $\approx$ = $\geq$ if $g'(-1/r) < 0$ and $\approx$ = $\leq$ if $g'(-1/r) > 0$. These inequalities allow us to find upper and lower bounds to the eigenvalues E_{nl} of H. It will be shown (Sect. 2) that the following compact expression may be written for these bounds

$$[1.6] \quad E_{nl} \approx \min_{r>0} \left\{ \frac{(n-l)^2}{r^2} - V(r) \right\}$$

with $\approx$ defined as for [1.5] above. Here, l is the angular momentum quantum number and $n = 1, 2, 3, \ldots$, counts the eigenvalues in each angular-momentum subspace.

The method of potential envelopes was developed in 1980 as a means of approximating the eigenvalues of the many-body problem (11). Since then it has been refined (1, 2, 12) and applied to a variety of problems (13–17).

2. The method of potential envelopes

We now present a brief account of envelope theory suitable for our application; a more complete account may be found in refs. 1 and 2. We suppose that the energy trajectories $H_{nl}(v)$ of the Schrodinger Hamiltonian $-\Delta + vh(r)$ are known exactly, where h is the *shape* of a central potential; the trajectory functions $H_{nl}(v)$ are restricted, if necessary, to those values of the coupling parameter v, which are sufficiently large for the corresponding discrete eigenvalue to exist. The quantum number n counts the eigenvalues in each angular-momentum subspace; eigenvalues so labelled have degeneracy exactly $(2l + 1)$.

We now consider a new Hamiltonian $-\Delta + V(r)$ in which the potential V is a smooth increasing transformation $V(r) = g(h(r))$ of the potential h. We assume that g is either convex or concave, that is to say either $g'' > 0$ or $g'' < 0$; these cases give rise, respectively, to lower and upper energy bounds. We can summarize the situation by the following two expressions:

$$[2.1] \quad -\Delta + vh(r) \rightarrow H_{nl}(v)$$

$$[2.2] \quad -\Delta + V(r) \rightarrow E_{nl}$$

For definiteness, we now suppose that g is concave so that $g'' < 0$. Because of the concavity of g we know that the tangent lines to g (as a function of h) all lie above g, and we can therefore write

$$[2.3] \quad V(r) = g(h(r)) \leq A + vh(r)$$

where, by calculus, we find

$$[2.4] \quad \begin{aligned} A &= g(h(t)) - h(t)g'(h(t)) \\ v &= g'(h(t)), \qquad t \in (0, \infty) \end{aligned}$$

$h(t)$ is the point of contact of $V(r)$ with its tangent potential

$$V^{(t)}(r) = A(t) + v(t)h(r)$$

Since the Hamiltonians we consider are self-adjoint and bounded below, we can employ the variational characterization of eigenvalues (18–20) to deduce that the potential inequality [2.3] implies the corresponding spectral inequality

$$[2.5] \quad E_{nl} \leq V(t) + H_{nl}(v(t))$$

that is to say

$$[2.6] \quad E_{nl} \leq g(h) - hg'(h) - H_{nl}(g'(h))$$

where $h = h(t)$. We now minimize the upper bound [2.6] by differentiating with respect to h and cancelling the factor $g''(h) < 0$ to obtain the critical point

$$[2.7] \quad h = H_{nl}[g'(h)]$$

In view of [2.6] and [2.7] and the known (1) concavity of trajectory functions like $H_{nl}(v)$, we can reformulate the expression for the best upper bound by a Legendre transformation as follows.

$$[2.8] \quad E_{nl} \leq \min_{r>0} \{K_{nl}(r) - V(r)\}$$

where

$$[2.9] \quad K_{nl}(r) = H_{nl}(u) - u H_{nl}(u), \qquad h(r) = H_{nl}(u)$$

The $K_{nl}(r)$ functions are well defined by [2.9] because H_{nl} is concave (1) so that H_{nl} is monotone and is invertible; they are positive definite and represent mean kinetic energies in the envelope approximation. We have used r in place of the parameter t since in the energy picture, there can be no confusion. What we have in [2.8] is a semiclassical approximation that is valid whenever the potential $V(r)$ is a concave transformation $g[h(r)]$ of the potential $h(r)$. If the transformation g is *convex*, then the inequalities are reversed and one obtains *lower* bounds. If the potential $V(r)$ depends on various parameters, then the dependence of the energies on these parameters is automatically given by the approximation [2.8]. A more general formulation of this geometrical theory described in ref. 2 allows also for *sums* of soluble potential terms.

As an example, we consider smooth transformations of the Coulomb potential $h(r) = -1/r$ for which we have

$$[2.10] \quad h(r) = \frac{-1}{r} \rightarrow H_{nl}(v) = -\left[\frac{v}{2(n-l)} \right]^2$$

From [2.9] we find that

$$K_{nl}(r) = \left[\frac{(n-l)}{r} \right]^2$$

Consequently [2.8] becomes

$$[2.11] \quad E \approx \min_{r>0} \left\{ \frac{(n-l)^2}{r^2} - V(r) \right\}$$

where $V(r) = g(-1/r)$; and $\approx$ = $\leq$ if g is concave, and $\approx$ = $\geq$ if g is convex. If the transformation function g is slowly varying, then, as we shall see, this simple formula is remarkably useful for it answers approximately the general question *How does the spectrum depend on the potential?* It is also interesting that the transformation function g does not itself appear in [2.11]; g is only used to establish the energy bounds.

3. The Coulomb-plus-Yukawa potential

For values of the parameter γ in the interval $\gamma < \beta$, the Coulomb-plus-Yukawa potential

TABLE 1. Eigenvalue upper bounds for the Hamiltonian $H = -\lambda - \beta/r + \gamma e^{-r}/r$ obtained by the method of potential envelopes, [2.11], along with accurate results computed numerically (in parentheses)

	$\beta = 1$		
	γ		
$n\,l$	-0.1	-0.5	-1.0
1 0	−0.257 20	−0.297 52	−0.389 89
	(−0.263 19)	(−0.332 19)	(−0.467 26)
2 0	−0.062 50	−0.062 52	−0.062 54
	(−0.063 92)	(−0.070 31)	(−0.079 52)
4 0	−0.015 63	−0.015 63	−0.015 63
	(−0.015 80)	(−0.016 53)	(−0.017 51)
5 0	−0.010 00	−0.010 00	−0.010 00
	(−0.010 09)	(−0.010 09)	(−0.010 95)
1 1	−0.062 50	−0.062 52	−0.062 54
	(−0.062 66)	(−0.063 33)	(−0.064 30)
2 1	−0.027 78	−0.027 78	−0.027 78
	(−0.027 83)	(−0.028 05)	(−0.028 36)
4 1	−0.010 00	−0.010 00	−0.010 00
	(−0.010 01)	(−0.010 06)	(−0.010 13)
5 1	−0.006 94	−0.006 94	−0.006 94
	(−0.006 95)	(−0.006 98)	(−0.007 02)

$$[3.1] \qquad V(r) = -\frac{\beta}{r} + \frac{\gamma}{r}e^{-r}, \qquad \beta > 0$$

is attractive and Coulombic for small r; for $\gamma > \beta$, $V(r)$ no longer looks Coulombic but resembles a molecular potential of the Kratzer variety (21). In this paper, only the case $\gamma < \beta$ will be studied, we therefore select the Coulomb potential as our basis potential $h(r) = -1/r$ and consequently represent $V(r)$ as a smooth transformation of $h(r)$ (as described in Sect. 2), that is to say

$$[3.2] \qquad V(r) = g\left(\frac{-1}{r}\right)$$

It is a simple matter to verify that for this choice of $h(r)$ and $\forall r > 0$ the transformation function g is *concave* for $\gamma < 0$, and *convex* for $0 < \gamma < \beta$. By [2.11] we know therefore that the corresponding Coulomb envelopes result in either upper or lower bounds to the energies. Thus we have

$$[3.3] \qquad E_{nl} \lessapprox \min_{r>0}\left\{\frac{(n-l)^2}{r^2} - \frac{\beta}{r} - \frac{\gamma}{r}e^{-r}\right\}$$

where $\lessapprox = \leqslant$ if $0 < \gamma < \beta$ and $\lessapprox = \geqslant$ if $\gamma < 0$.

Since the approximation is based on the Coulomb potential, however, this implies that the approximate spectrum inherits the degeneracies of the hydrogenic atom. Thus, even though the actual spectrum $\{E_{nl}\}$ does not share this Coulomb degeneracy, our *approximate* spectrum provides the same bound for each set of eigenvalues with $(n - l) =$ constant.

In Table 1 some results are displayed for various values of the potential parameters and of (n,l) along with some accurate numerical results. These latter results were obtained by a finite-element method that was implemented on a microcomputer. As can be seen, our results are quite good for small values of the Yukawa coupling constant γ. The accuracy increases with increasing (n,l).

TABLE 2. Bound-state eigenvalue upper bounds for the Yukawa potential $V(r) = -2\alpha Z e^{-\lambda r}/r$ in kiloelectronvolts (neutral atoms), along with the results of the shifted $1/N$ approximation of Dutt *et al.* (9) and those of McEnnan *et al.* (22) (labelled 'Analytic perturbation'), numerical results are presented for comparison. The Yukawa potential corresponds to the case $\beta = 0$ for the Coulomb-plus-Yukawa potential

Z	$n\,l$	Envelope	Shifted $1/N$	Analytic perturbation	Numerical
13	1 0	−1.450	−1.488	−1.484	−1.488
36	1 0	−14.16	−14.24	−14.24	−14.24
	2 0	−1.437	−1.676	−1.615	−1.692
	1 1	−1.437			−1.566
79	1 0	−74.80	−74.91	−74.95	−74.95
	2 0	−12.00	−12.49	−12.45	−12.50
	1 1	−12.00			−12.25

The special case (22) $\beta = 0$, $\gamma = -2\alpha Z$, $\lambda = 1.13\alpha Z^{1/3}$ where $\alpha = (137.037)^{-1}$ is the fine-structure constant and Z the atomic number, reduces $V(r)$ to the Yukawa potential $V(r) = (-2\alpha Z e^{-\lambda r})/r$. This is the form taken by the Yukawa potential in atomic-physics applications and is appropriate for modeling the energy levels of neutral atoms. The method of potential envelopes was applied to this potential by one of us in an earlier paper (16). We now clarify how the energies obtained from [2.11] are related to our results in kiloelectronvolts. For $Z = 1$ and $\lambda = 0$, $V(r) \to -2\alpha/r$, resulting in the hydrogenic spectrum,

$$[3.4] \qquad E_{nl} = \frac{-\alpha^2}{(n-l)^2}$$

Thus, the conversion factor from E_{nl} to energies in kiloelectronvolts is given by the relation

$$[3.5] \qquad \text{Energy} = \left(\frac{13.6047}{1000\alpha^2}\right)E_{nl} \qquad \text{keV}$$

$$= 255.485\,E_{nl} \qquad \text{keV}$$

Employing the shifted large-N approximation Dutt *et al.* (9) also calculated the bound-state energies. McEnnan *et al.* (22) used perturbation theory to do the same. Hall's (16) bounds on E_{nl} along with the results of Dutt *et al.* and those of McEnnan *et al.* are presented in Table 2. The results of Dutt *et al.* and McEnnan *et al.* are of higher accuracy than those that we found with the aid of potential envelopes, however the computational effort required is correspondingly much more.

4. Comparison of potential envelopes and a variational method

To compare our results with those of Adamowski (8) we adopt his scale of units for the length (r) and energy. With $\beta = 2$, $\gamma < \beta$, and $\lambda > 0$, we have

$$[4.1] \qquad V(r) = -\frac{2}{r} - \frac{\gamma}{r}e^{-\lambda r}$$

Adamowski obtained very accurate results by using a 10-parameter trial wave function. In fact, to the precision quoted,

TABLE 3 Some eigenvalue upper bounds for the Coulomb-plus-Yukawa potential as functions of λ, for γ = −1 and γ = −10, obtained with [2.11] For comparison, the variational results from ref. 8 are given in parentheses

	γ = −1					
	λ					
n l	0 01	0 05	0.1	0 2	0.5	1 0
1 0	−2 240 03 (−2.240 05)	−2.200 82 (−2.201 22)	−2.153 26 (−2 154 79)	−2.062 78 (−2.068 40)	−1 825 31 (−1.853 02)	−1.525 78 (−1.601 49)
2 0	−0.552 63 (−0.552 70)	−0 515 69 (−0.517 14)	−0 474 78 (−0 479 84)	−0.408 16 (−0.423 73)	−0.297 52 (−0.340 92)	−0.255 20 (−0.302 13)
4 0	−0.131 14 (−0 131 38)	−0.102 04 (−0.106 02)	−0.080 66 (−0 090 15)	−0 065 63 (−0 078 69)	−0.062 52 (−0 071 39)	−0.062 50 (−0.068 30)
1 1	−0.552 63 (−0 552 70)	−0 515 69 (−0.517 14)	−0 474 78 (−0 479 84)	−0 408 16 (−0.423 73)	−0.297 52 (−0.340 92)	−0.255 20 (−0.302 13)
2 1	−0.240 29 (−0 240 40)	−0 206 84 (−0 209 00)	−0 175 25 (−0.181 72)	−0.137 28 (−0.151 44)	−0 112 46 (−0 125 96)	−0 111 13 (−0 116 35)

	γ = −10					
	λ					
n l	0 01	0.05	0.1	0.2	0.5	0.85
1 0	−35 9001 (−35 9001)	−35 5021 (−35 5031)	−35.0083 (−35.0124)	−34.0330 (−34.0489)	−31.2030 (−31 2967)	−28.0768 (−28.3300)
2 0	−8 9003 (−8 9005)	−8 5082 (−8.5122)	−8 0326 (−8.0482)	−7.1281 (−7 1862)	−4.7613 (−5 0617)	−2.6037 (−3.2972)
4 0	−2.1513 (−2.1520)	−1.7820 (−1.7966)	−1.3737 (−1.4254)	−0.7185 (−0.8800)	−0 0627 (−0.2431)	−0.0625 (−0.1503)
1 1	−8 9003 (−8 9004)	−8.5082 (−8.5102)	−8 0300 (−8.0404)	−7 1280 (−7.1569)	−4.7613 (−4.9105)	−2.6037 (−2.9522)
2 1	−3.9007 (−3.9010)	−3.5183 (−3.5251)	−3 0717 (−3.0968)	−2.2761 (−2.3638)	−0.5952 (−0 9507)	−0 1117 (−0.3367)

his results are about as accurate as those obtained by integrating the Schrödinger equation numerically Table 3 contrasts our results with those of Adamowski. As is evident, potential envelopes give good results for a wide range of potential parameters. Though the accuracy of Adamowski's results is in general superior to that of the potential-envelope method, this is not always the case. For instance, for small values of the screening parameter λ of the Yukawa component, our results are just as accurate This is due to the similarity in shape of the Coulomb-plus-Yukawa and the Coulomb potential (which we employ as our basis potential) for this range of λ.

5. Conclusion

The method of potential envelopes was used to develop a simple formula for approximating the bound state eigenvalues E_{nl} of the Coulomb-plus-Yukawa potential. This formula yields energy bounds that are functions of the potential parameters (β,γ,λ). Our results are good approximations to the true eigenvalues for a wide range of the potential parameters and for all values of (n,l). As n or l increases the bounds improve Unfortunately, the approximate spectrum shares the degeneracy particular to the Coulomb potential, that is to say, we get a single bound for each set of eigenvalues with the same values for $(n - l)$.

With each eigenvalue bound is associated a shifted Coulomb potential

$$A(t) + v(t)\left(\frac{-1}{r}\right)$$

Such a potential gives rise to a wave function. As a result, we have at our disposal a collection of Coulomb wave functions each of which is independently scaled in an optimal fashion. These can be used either as the basis for a Rayleigh–Ritz computation or to estimate other physical quantities.

In this paper we have investigated the spectrum of the Coulomb-plus-Yukawa potential for the range $\gamma < \beta$ of the potential parameters β and γ. The range $\gamma > \beta$ leads to potentials $V(r)$ with a positive pole at the origin, as required by molecular systems. In this region, the hydrogenic potential would only be suitable as a basis potential $h(r)$ in cases where the coupling was very weak. To use the method of potential envelopes effectively one could perhaps use for $h(r)$ a more appropriate potential such as the Kratzer molecular potential, which has a pole at the origin and for which exact eigenvalues are known (21).

The method of potential envelopes is particularly useful for approximating the eigenenergies corresponding to a potential $V(r) = g[h(r)]$ for which the convexity of the transformation function g is *definite* (i.e., either $g'' > 0$ or $g'' < 0$). In these cases the approximate eigenvalues, which in general are given simply by the minimization of a function of one variable, are also *bounds* on the exact eigenvalues E_{nl}. The main purpose of this global approximation theory is to provide a tool for explor-

ing the parameter space of the problem prior to more specific numerical calculations

Acknowledgments

Partial financial support of this work by the Natural Sciences and Engineering Research Council of Canada under Grant No. 0GP0003438 is gratefully acknowledged.

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