PHYSICAL REVIEW A VOLUME 32, NUMBER 1 JULY 1985

Envelope representations for screened Coulomb potentials

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(Received 11 January 1985)

We study the discrete eigenvalues E_{nl} of the Schrödinger Hamiltonian $H=-\frac{1}{2}\Delta+V(r)$, where $V(r)=g(-1/r)$ is an increasing concave transformation of the Coulomb potential, and n is the principal (radial) quantum number. It is demonstrated by the method of potential envelopes that upper bounds are provided by the simple formula $E_{nl}\leq \min_{s>0}\{\frac{1}{2}s+V((n+l)/s^{1/2})\}$, where s is a real variable. Numerical results are compared with previous work for two specific screened Coulomb potentials. In the case of the Yukawa potential $V(r)=-(v/r)\exp(-\lambda r)$, it is shown that the inequality $(n+l)^2\lambda/v<2/e$ is sufficient to guarantee the existence of the eigenvalue E_{nl}: In the case of S states, sharp upper and lower bounds are also provided by a different method.

I. INTRODUCTION

We study the discrete spectra of Schrödinger Hamiltonians of the form

$$H=-\tfrac{1}{2}\Delta+V(r),\quad V(r)=g(-1/r)\ , \qquad (1.1)$$

where the smooth transformation function $g(X)$ is increasing and concave for $X=-1/r<0$. Various screened Coulomb potentials used in atomic and nuclear physics have this representation. Two examples which we shall look at and for which there are recent comparable studies[1,2] in the atomic physics literature are given by

$$V_1(r)=-(v/r)[1-r\lambda(1-1/Z)/(1+r\lambda)] \qquad (1.2)$$

and the Yukawa potential

$$V_2(r)=-(v/r)\exp(-\lambda r)\ . \qquad (1.3)$$

In the atomic physics applications the coupling constant v and the range parameter λ for the non-Coulomb factor are given by

$$v=\alpha Z,\quad \lambda=\lambda_0\alpha Z^{1/3}\ , \qquad (1.4)$$

where $\alpha=(137.037)^{-1}$ is the fine-structure constant and Z is the atomic number. In terms of our notation the values of λ_0 used in the two potentials in Refs. 1 and 2 are, respectively, 0.98 and 1.13.

Since our methods may still be unfamiliar, it is necessary to make it quite clear how we proceed from the formulation to the results quoted in keV. We take care of this detail immediately. Since for $Z=1$ and $\lambda=0$ both potentials lead to the hydrogenic spectrum

$$E_{nl}=-\alpha^2/2(n+l)^2\ , \qquad (1.5)$$

it follows in general that the energies in keV are obtained by the relation

$$\begin{aligned}\text{Energy }&=(2\times 13.6047/1000\alpha^2)E\text{ keV}\\ &=510.969E\text{ keV}\ . \end{aligned} \qquad (1.6)$$

It is straightforward to show that both $V_1(r)$ and $V_2(r)$ have the representation $V(r)=g(-1/r)$ where $g(X)$ satisfies $g'(X)>0$ and $g''(X)<0$ for $X<0$. What we now have to say applies to this whole class of potentials of which $V_1(r)$ and $V_2(r)$ are simply illustrations. The significance of this representation for the potential is that $V(r)$ is the envelope of a family $\{V^{(t)}(r)\}$ of "tangential" Coulomb potentials each of which has the form

$$V^{(t)}(r)=A(t)+v(t)(-1/r)\geq V(r)\ . \qquad (1.7)$$

The potential inequality in (1.7) is a consequence of the concavity of the transformation function g and it allows us to find upper bounds to the eigenvalues E_{nl} of H. In fact, these upper bounds may be written in the simple compact form

$$E_{nl}\leq \min_{s>0}\{\tfrac{1}{2}s+V((n+l)/s^{1/2})\}\ , \qquad (1.8)$$

where $n=1,2,3,\ldots$, is the radial quantum number and l is the angular momentum quantum number (the upper bound has identical degeneracies to those of the pure hydrogenic spectrum). The approximation (1.8) reduces the Schrödinger eigenvalue problem to an exercise in the calculus of a function of a single real variable s which equals the mean kinetic energy. Even the transformation function g has vanished and all that remains is the original potential $V(r)$ carrying with it the dependence of the eigenvalues on all the potential parameters. Most of the results of this paper are obtained from this single equation.

The method of potential envelopes was introduced[3] in 1980 as a technique for approximating the eigenvalues of the many-body problem. The method applies equally well to envelopes of arbitrary soluble potentials. When g is *convex,* the method yields energy *lower* bounds. The theory has been extended to allow for sums of soluble potentials[4] and the formulation has been streamlined by the introduction,[5] refinement,[6] and application[7] of the concept of "kinetic potentials." However, in order to make the present article essentially self-contained, we give in Sec. II below a brief derivation of the principal special result (1.8) used in this paper.

This simple upper bound is particularly appropriate for the screened Coulomb potentials of atomic physics because of the close relationship in these cases of $V(r)$ to the hydrogen-like potential. This general observation is supported by our specific results for the potentials $V_1(r)$ and $V_2(r)$ which are discussed in Secs. III and IV.

For the Yukawa potential $V_2(r)$ our upper bound (1.8) allows us to determine the following sufficient condition for the existence of the discrete eigenvalue E_{nl}:

$$(n+l)^2\lambda/v < Q = 2/e = 0.7357 \ . \tag{1.9}$$

For the Yukawa potential $V_2(r)$ we are also able to find (by an independent method) simple explicit recipes for upper and lower bounds to the S-state eigenvalues. In these cases we get the stronger critical binding result Eq. (1.9) with $Q=1$.

II. THE METHOD OF POTENTIAL ENVELOPES

We now present a brief argument leading to Eq. (1.8) which is the key result used in this paper. A more complete discussion of this geometrical theory may be found in Refs. 5 and 6.

We suppose that we can solve Schrödinger's equation for the discrete eigenvalues when the potential is $vh(r)$ and we wish to estimate the eigenvalues when the potential is changed to $g(h(r))$ where g is monotone increasing and concave. We summarize this situation by the relations

$$-\tfrac{1}{2}\Delta + vh(r) \rightarrow \mathscr{E}_{nl}(v) \ , \tag{2.1}$$

$$-\tfrac{1}{2}\Delta + g(h(r)) \rightarrow E_{nl} \ . \tag{2.2}$$

Of course, discrete eigenvalues may not exist for all values of the coupling v but we assume, for v sufficiently large, that there are some. Because of the concavity of g, the tangent lines to g (as a function of h) all lie above g and we can immediately find by calculus that

$$g(h(r)) \le A + vh(r) \ , \tag{2.3}$$

where

$$A = g(h(t)) - h(t)g'(h(t)) \quad \text{and} \quad v = g'(h(t)) \ , \qquad t \in (0,\infty) \tag{2.4}$$

and $h(t)$ is the point of contact of $V(r)=g(h(r))$ with its "tangential 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 the eigenvalues[8] to derive the "comparison theorem" of quantum mechanics which tells us that the potential inequality (2.3) implies the spectral inequality

$$E_{nl} \le A(t) + \mathscr{E}_{nl}(v(t)) \ . \tag{2.5}$$

We now minimize the right-hand side of (2.5). We can work now with the variable h since the upper bound is a function of h.

The necessary condition for a minimum is obtained by differentiation with respect to h and cancellation of the factor $g''(h)<0$ (by hypothesis, g is concave). This yields the critical point

$$h = \mathscr{E}'_{nl}(v) \ . \tag{2.6}$$

For our very specific application we have $h(r)=-1/r$ and we therefore know that the corresponding "energy trajectory" function $\mathscr{E}_{nl}(v)$ is concave and is given explicitly by

$$h(r) = -1/r \rightarrow \mathscr{E}_{nl}(v) = -v^2/2(n+l)^2 \ . \tag{2.7}$$

This concavity property of energy trajectories is actually true much more generally (see Ref. 5, theorem 2). We can therefore use (2.6) to recast the minimization of (2.5) in the new form

$$E_{nl} \le \min_{v>0} \{ \mathscr{E}_{nl}(v) - v\mathscr{E}'_{nl}(v) + g(\mathscr{E}'_{nl}(v)) \} \ . \tag{2.8}$$

This formulation of the method is actually interesting for it tells us (approximately) how the eigenvalues E_{nl} derived from the potential $V(r)=g(h(r))$ depend on the energy trajectories $\mathscr{E}_{nl}(v)$ corresponding to the potential $vh(r)$. The final step to Eq. (1.8) is made by a (further) Legendre transformation[9] defined by

$$\tfrac{1}{2}s = \mathscr{E}_{nl}(v) - v\mathscr{E}'_{nl}(v), \quad \bar{h}_{nl}(s) = \mathscr{E}'_{nl}(v) \tag{2.9}$$

which leads to the result

$$E_{nl} \le \min_{s>0} \{ \tfrac{1}{2}s + g(\bar{h}_{nl}(s)) \} \ . \tag{2.10}$$

The functions $\bar{h}_{nl}(s)$ are called kinetic potentials and for our particular problem where $h(r)=-1/r$ we have from (2.7) and (2.9) that the Coulomb kinetic potentials are given by

$$\bar{h}_{nl}(s) = -s^{1/2}/(n+l) \ . \tag{2.11}$$

Now we see that (2.10) and (2.11) immediately lead to (1.8) because $V(r)=g(h(r))=g(-1/r)$ so that $g(\bar{h}) = V(-1/\bar{h})$. A table of kinetic potentials may be found in Ref. 5 and a formulation of the problem starting with an abstract definition of kinetic potentials may be found in Ref. 6.

III. THE SCREENED COULOMB POTENTIAL $V_1(r)$

The potential studied by Mehta and Patil[1] is given by

$$V_1(r) = -(v/r)[1 - r\lambda(1-1/Z)/(1+r\lambda)] \tag{3.1}$$

with

$$v = \alpha Z \quad \text{and} \quad \lambda + 0.98\alpha Z^{1/3} \ . \tag{3.2}$$

It is a matter of personal taste whether one keeps the vestigial factor of $\frac{1}{2}$ in front of the Laplacian in the Schrödinger Hamiltonian. In the present paper we have chosen to keep this factor so that we can relate our work to Refs. 1 and 2 within a common framework. Mehta and Patil choose to absorb this factor and also the fine-structure constant into the units they use. Anyway, with the potential defined by (3.1) and (3.2) and the keV factor given in (1.6) it is evident that we are discussing the same problem.

The potential (3.1) is almost Coulombic everywhere for it is like $-v/r$ for small r and like $-v/Zr$ for large values of r. This makes our present approach based on Coulomb envelopes very appropriate. The simplest way to obtain results is to use Newton's method to find the

TABLE I. Some energies E_{nl} (in keV) corresponding to the screened Coulomb potential $V_1(r)$ with $\lambda_0=0.98$. Our envelope results are upper bounds. Variational results are from Ref. 1.

	E_{10}		E_{20}	
Z	Envelope	Variational	Envelope	Variational
14	-1.952	-1.94	-0.187	-0.161
19	-3.786	-3.77	-0.423	-0.394
24	-6.254	-6.20	-0.779	-0.745
29	-9.364	-9.28	-1.262	-1.22
34	-13.12	-13.1	-1.879	-1.82
39	-17.53	-17.4	-2.633	-2.59
44	-22.59	-22.5	-3.528	-3.44
49	-28.30	-28.3	-4.566	-4.50
54	-34.67	-34.6	-5.748	-5.67
59	-41.70	-41.6	-7.078	-7.01
64	-49.39	-49.4	-8.556	-8.46
69	-57.74	-57.7	-10.18	-10.1
74	-66.76	-66.6	-11.96	-11.8
79	-76.43	-76.3	-13.89	-13.8
84	-86.77	-86.6	-15.97	-15.8

critical point and consequently the minimum in Eq. (1.8). We display some results for $Z=14$—84 (by increments of 5) in Table I. These results by the method of potential envelopes are of course upper bounds and it turns out that they are in every case lower than the corresponding variational results of Ref. 1 which are also displayed in the table.

We do not quote the numerical results obtained by the analytical method of Ref. 1 because we are not sure how they relate to the exact eigenvalues. Mehta and Patil discuss the linear-plus-Coulomb potential in the same paper. We have also applied our geometrical methods to this potential: in Refs. 6 and 7 upper and lower bounds and a simple eigenvalue formula are given for this interesting problem.

IV. THE YUKAWA POTENTIAL $V_2(r)$

In a recent paper by McEnnan *et al.*[2] the Yukawa potential given by

$$V_2(r)=-(v/r)\exp(-\lambda/r)\ , \qquad (4.1)$$

with

$$v=\alpha Z,\ \ \lambda=1.13\alpha Z^{1/3} \qquad (4.2)$$

is applied to atomic physics. Many other things which we do not refer to here are done in this substantial paper. Our purpose is simply to offer two simple ways to approximate the eigenvalues of the Yukawa problem and we use the results of these authors to provide a comparison. In Table II we exhibit our envelope upper bounds for the eigenvalues studied by these authors, along with their most accurate results under the heading "Numerical." Our upper bound has the same degeneracies as the hydrogenic atom so that we obtain the same bound for each collection of eigenvalues E_{nl} with "the principal quantum number" $(n+l)$ constant. This quantity is, of course, not a constant of the motion for the Yukawa problem and the numerical results of McEnnan *et al.* do separate the eigenvalues. Since our results are so easily obtained from Eq. (1.8) and they turn out to be good approximations, we only quote a few results for eigenvalues not mentioned by McEnnan *et al.* For these weakly bound states another approximation obtained by a distinct method seems to be very useful.

We found this approximation by exploiting the known[10] exact solution for the S states of the Hulthén potential. We write these, first of all, in terms of new range and coupling parameters b and u. Thus we have

$$-\tfrac{1}{2}\Delta-u(e^{r/b}-1)^{-1}\rightarrow E_{n0}=-(2ub^2-n)^2/8n^2b^2\ , \qquad (4.3)$$

where the radial quantum number $n=1,2,3,\ldots$. Now whilst the simple Yukawa-Hulthén inequality

$$-\exp(-\lambda r)/r\geq-\lambda[\exp(\lambda r)-1]^{-1} \qquad (4.4)$$

is valid, it is not tight enough to lead to a useful spectral approximation. However, we are able to establish the following sharper inequalities:

$$0\leq f(x)=e^{-x}/x-e^{-x}/\sinh(x)<0.056,\ \ x>0\ . \qquad (4.5)$$

The left-hand inequality is immediate because we know that $\sinh(x)\geq x$. The right-hand inequality is found (in the modern way, with the help of a microcomputer) by

TABLE II. Some energies E_{nl} (in keV) corresponding to the Yukawa potential $V_2(r)$ with $\lambda_0=1.13$. Our envelope results are upper bounds. The E lower and E upper are the S-state bounds provided by our formula (4.7). Numerical results are from Ref. 2.

Z	n	l	Envelope	E lower	E upper	Numerical
13	1	0	-1.450	-1.508	-1.455	-1.488
	2	0		-0.0718	-0.0191	
36	1	0	-14.16	-14.37	-14.16	-14.24
	2	0	-1.437	-1.715	-1.510	-1.692
	1	1	-1.437			-1.566
	3	0		-0.214	-0.00884	
79	1	0	-74.80	-75.39	-74.80	-74.95
	2	0	-12.00	-12.67	-12.08	-12.50
	1	1	-12.00			-12.25
	3	0	-1.559	-2.474	-1.890	
	4	0		-0.585	-0.00178	

simply plotting $f(x)$. This graph is shown in Fig. 1. The maximum lies between 0.055 and 0.056 so that the latter number is a safe upper bound. If we now write $x=\lambda r$ then (4.5) becomes

$$-2B(e^{2\lambda r}-1)^{-1}-B(0.056)\le -Be^{-\lambda r}/\lambda r \le -2B(e^{2\lambda r}-1)^{-1},\quad B>0\,. \tag{4.6}$$

If we now use the spectral comparison theorem and choose $u=2B=2v\lambda$ and $b=1/2\lambda$ in (4.3) we obtain finally

$$-(v-n^2\lambda)^2/2n^2-(0.056)\lambda v\le E_{nl}\le -(v-n^2\lambda)^2/2n\,, \tag{4.7}$$

as lower and upper bounds on the S-state eigenvalues of the Hamiltonian $-\frac{1}{2}\Delta-ve^{-\lambda r}/r$. The numerical implications are quite interesting as the results in Table II clearly show. A useful approximation for the S states is the average of these bounds which gives

$$E_{n0}\simeq E_{\approx}=-(v-n^2\lambda)^2/2n^2-(0.028)\lambda v\,. \tag{4.8}$$

The error in the approximation $E_{\approx}$ for the Yukawa eigenvalues is always less than $(0.028)\lambda v$.

We now look at the question of critical binding. Because the Yukawa potential has a finite range λ^{-1} there may only be a few bound states corresponding to given values of the parameters v and λ. For the Yukawa problem Eq. (1.8) takes the form

$$E_{nl}\le \min_{s>0}\{E(s)\}\,, \tag{4.9}$$

where

$$E(s)=\{\tfrac{1}{2}s-vs^{1/2}\exp[-\lambda(n+l)/s^{1/2}]/(n+l)\}\,.$$

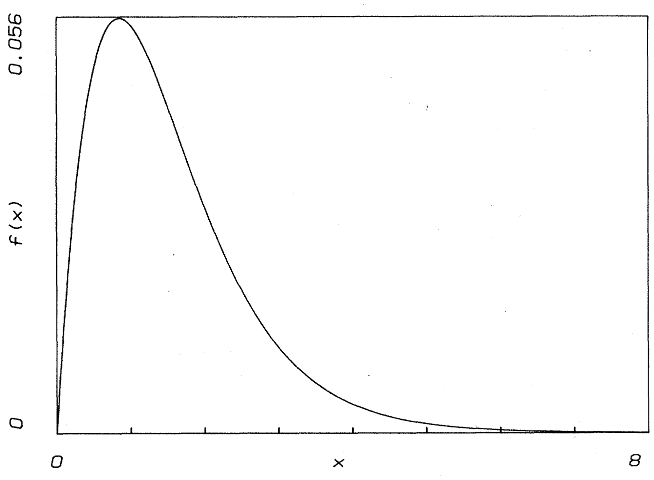

FIG. 1. Graph of the function $f(x)=e^{-x}/x-e^{-x}/\sinh(x)$ which has the upper bound 0.056. This bound allows us to obtain the upper and lower bounds (4.7) for the eigenvalues corresponding to the Yukawa potential.

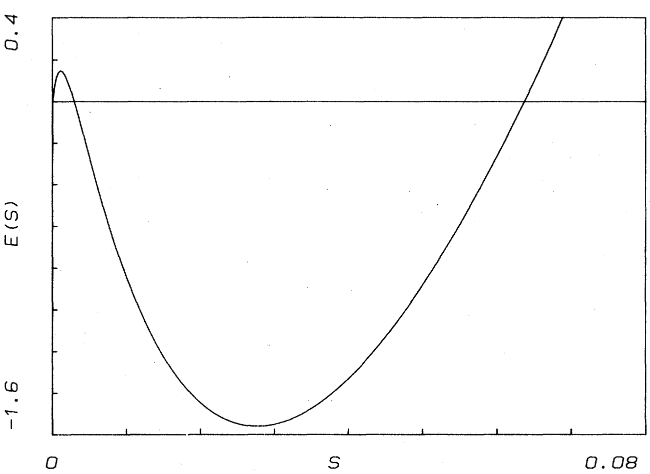

FIG. 2. The graph of $E_{30}(s)$ corresponding to the Yukawa potential for gold ($Z=79$). The minimum value -1.559 of this graph, as quoted in Table II, is our upper bound for the eigenvalue E_{30}. A simple routine based on Newton's method determines these minima very quickly.

The graph $E(s)$ has two critical points and this is illustrated in Fig. 2: the larger value of s leads to the minimum which we seek. The critical points are given analytically by the equation $E'(s)=0$ which (after a little simplification) becomes

$$\lambda(n+l)^2/v=e^{-x}(x+x^2),\quad x=\lambda(n+l)/s^{1/2}\,. \tag{4.10}$$

The maximum 0.839 962 of the right-hand side of (4.10) for positive x occurs at $x_1=\frac{1}{2}(1+5^{1/2})$. Hence we obtain the following necessary condition for the existence of the minimum value:

$$\lambda(n+l)^2/v<e^{-x_1}(x_1+x_1^2)\simeq 0.83996\,. \tag{4.11}$$

However, this condition is not sufficient for the existence of discrete eigenvalues because $E(s)$ may turn out to be positive. If we substitute (4.11) in (4.9) then we find for the critical value of s (in terms of x)

$$E(s)=-\tfrac{1}{2}\lambda^2(n+l)^2[(1-x_1)/x_1^2(1+x_1)]\,. \tag{4.12}$$

Consequently, we require also that $x_1=\lambda(n+l)/s^{1/2}<1$. Combining these results we find the following *sufficient condition* for the existence of the discrete Yukawa eigenvalue E_{nl} of the Hamiltonian $H=-\frac{1}{2}\Delta-v\exp(-\lambda r)/r$:

$$\lambda(n+l)^2/v<Q=2/e\simeq 0.73576\,. \tag{4.13}$$

From the upper inequality in (4.7) we get the stronger result $Q=1$ for the S states ($l=0$).

V. CONCLUSION

We have shown that the Schrödinger eigenvalues corresponding to a family of screened Coulomb potentials can be closely approximated by minimizing the function $E(s)=\frac{1}{2}s+V[(n+l)/s^{1/2}]$ with respect to the real kinetic energy variable s. The remarkable fact is that these minima are eigenvalue *upper bounds* which indicate approximately how the eigenvalues E_{nl} depend on all the potential parameters. The main purpose of this geometrical approach is to provide analytical tools which will allow general exploration prior to the determination of very accurate specific results by direct numerical methods. For each upper bound, the value of s specifies through the equation $\bar{h}_{nl}(s)=h(t)$ and Eq. (2.3) a particular shifted potential $A(t)+v(t)h(r)$. For the Coulomb envelopes which we have studied in this article, we have $h(t)=-1/t$ and $\bar{h}_{nl}(s)=-s^{1/2}/(n+l)$, and consequently $t=(n+l)/s^{1/2}$. Thus, in addition to the eigenvalue bounds, we also obtain a collection of Coulomb wave functions (each differently and optimally scaled) which can be used either for the estimation of other physical quantities or as the basis for a Rayleigh-Ritz computation.

We do not mention the experimental data in this article nor do we try to choose between the two potentials we have used as illustrations. The parameters $v=\alpha Z$ and $\lambda=\lambda_0\alpha Z^{1/3}$ have been given "physical" values in order to allow comparison with the literature and also to show that the results of the geometrical approach are good in relevant domains. Of course, in addition to the solution of a simple eigenvalue problem, a full discussion of the atomic physics involves many other issues not the least of which is the question of relativistic effects. It is our wish that the simple tool we offer here will be used to help with this task. Now that physics is actively engaged in the world of nonlinear phenomena, it is perhaps more sharply realized than ever before just how important it is to exploit to the fullest any exact solutions to important problems that we are fortunate to have found. Geometrical methods, of course, are particularly suitable for implementing this program.

ACKNOWLEDGMENTS

The author would like to thank the Natural Sciences and Engineering Research Council of Canada for partial financial support of this work by Grant No. A3438. He would also like to thank the Department of Physics of the National Taiwan University in Taipei for its hospitality during a visit when some of this work was carried out.

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