PHYSICAL REVIEW A
GENERAL PHYSICS

THIRD SERIES, VOLUME 35, NUMBER 4 FEBRUARY 15, 1987

Modified Coulomb potentials with analytic energy levels: A semiclassical derivation

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(Received 8 September 1986)

A semiclassical analog to the Abraham-Moses-Gel'fand-Levitan method for generating radial potentials with analytic sets of energy levels is presented. The algorithm begins with the selection of a model potential whose energy levels can be expressed as analytic functions of the corresponding quantum numbers. Then, a finite number of states is deleted from its spectrum, leaving all the others unchanged. Subsequently, the incomplete spectrum is analytically inverted using a generalized version of the Rydberg-Klein-Rees equations. The result is a family of potential functions that, when quantized, give rise to the incomplete spectra. Emphasis is placed on the application of this method to a Coulomb model potential. The simple l-dependent analytic functions obtained allow the straightforward calculation and systematic study of a number of members of this modified Coulomb-potential family. The connection between these modifications and atomic pseudopotentials is also discussed.

I. INTRODUCTION

The rather limited number of potentials that can be solved exactly has been greatly enlarged with the recent introduction of a potential-function-generating algorithm by Abraham and Moses (AM).[1] Basically, the algorithm begins with the selection of a potential function with known analytical solutions. Then, the Gel'fand-Levitan[2] formalism is used to add or remove any particular eigenstate, leaving all the others unchanged. The result is a new potential function of the form

$$V(r)=V_0(r)+V'(r)\ , \tag{1}$$

where $V_0(r)$ is the original potential and $V'(r)$ is the AM modification. When quantized, the potential given above yields a spectrum which coincides with that of V_0, except for the added or deleted eigenstate. In another version of the algorithm, the modified potential is obtained by changing the normalization of a finite number of eigenfunctions.

The purpose of the present paper is to investigate an alternate method, based on semiclassical physics, for generating exactly solvable radial potentials. The method is analogous to the one proposed by Abraham and Moses[1] in that a finite number of states is deleted or added to the spectrum of a model potential. The basic ideas of this semiclassical approach have been briefly discussed in a study of the unfolding of experimental energy levels to determine pseudopotentials.[3] This paper, however, presents these ideas in a more general context, reviews and clarifies the fundamental concepts involved, and addresses some natural questions that might be raised concerning the semiclassical nature of the method. From the outset, attention is focused on modifications to the Coulomb potential and the connection between these modifications and pseudopotentials. A radial harmonic-oscillator potential is briefly discussed in the Appendix.

II. BASIC EQUATIONS

The semiclassical method proposed here for generating radial potential functions with analytic spectra is based on a generalized version of the well-known Rydberg-Klein-Rees[4] (RKR) inversion technique. Consequently, it would be instructive to begin with a brief review of the main steps involved in the derivation of the RKR equations, originally developed for application to diatomic molecules. Details of this derivation will facilitate the straightforward introduction of the generalizations. Consider Fig. 1(a) which shows an effective radial potential energy function

$$\Phi(r)=V(r)+\lambda/2r^2\ , \tag{2}$$

assumed to give rise to bound-state eigenvalues (atomic units will be used throughout this paper). Here $\lambda=l(l+1)$, and l is the angular momentum quantum number. A quantity of interest is the shaded area enclosed by a horizontal line representing some energy level E and the $\Phi(r)$ curve,

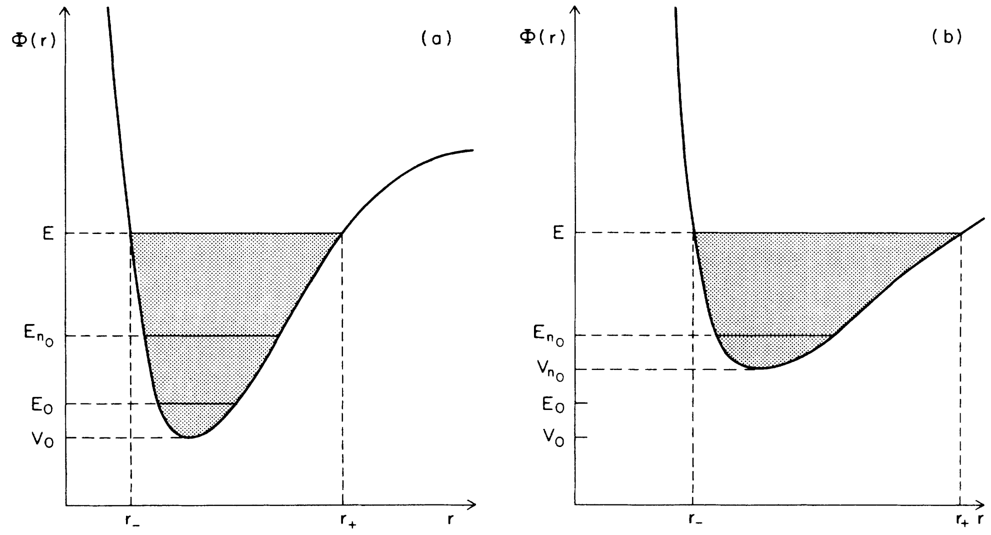

FIG. 1. Schematic representation of the semiclassical method for generating modified potentials with analytic energy spectra. The algorithm begins with a model effective potential (a) whose energy levels are given by analytic functions of the radial and angular momentum quantum numbers. The ground-state energy of this model potential is denoted by E_0. Then, a finite number of states is deleted from the lower end of the spectrum. After deleting enough levels to make E_{n_0} the new ground state, the incomplete spectrum is semiclassically inverted, with the result that the potential in (a) becomes modified as shown in (b). The energy levels lying above E_{n_0} are not perturbed and are given by the same analytic formula for both potentials.

$$\mathscr{A}=\int_{r_-}^{r_+}[E-\Phi(r)]dr\ . \tag{3}$$

The limits of integration are the classical turning points, defined by the roots of $\Phi(r_\pm)=E$. This area is an important quantity since we can obtain the width of the effective potential at E by differentiating it with respect to energy; that is,

$$\left.\frac{\partial\mathscr{A}}{\partial E}\right|_{\lambda}=r_+-r_- \tag{4}$$

for some given value of angular momentum. Similarly, differentiating with respect to λ,

$$\left.-2\frac{\partial\mathscr{A}}{\partial\lambda}\right|_{E}=r_-^{-1}-r_+^{-1}\ , \tag{5}$$

yields the difference between the reciprocals of the turning points.

Next, area $\mathscr{A}$ is transformed into a double integral by means of a Euler integral of the second kind

$$[E-\Phi(r)]=\frac{2}{\pi}\int_{\Phi(r)}^{E}\{(E-E')/[E'-\Phi(r)]\}^{1/2}dE'\ . \tag{6}$$

We obtain the result

$$\mathscr{A}=\frac{2}{\pi}\int_{r_-}^{r_+}\int_{\Phi(r)}^{E}\{(E-E')/[E-\Phi(r)]\}^{1/2}dE'\,dr\ . \tag{7}$$

Reversing the order of integration we write

$$\mathscr{A}=\frac{2}{\pi}\int_{V_0}^{E}(E-E')^{1/2}\left[\int_{r_-}^{r_+}[E'-\Phi(r)]^{-1/2}dr\right]dE'\ , \tag{8}$$

where V_0 is the value of the minimum of the effective potential. At this point we invoke the semiclassical JWKB quantization condition

$$(n+\tfrac{1}{2})\pi=2^{1/2}\int_{r_-}^{r_+}[E-\Phi(r)]^{1/2}dr\ , \tag{9}$$

from which we obtain the semiclassical density of states,

$$\frac{\partial n}{\partial E}=2^{-1/2}\pi^{-1}\int_{r_-}^{r_+}[E-\Phi(r)]^{-1/2}dr\ . \tag{10}$$

Here n is the radial quantum number. Using this result in Eq. (8) yields

$$\mathscr{A}=2^{3/2}\int_{V_0}^{E}(E-E')^{1/2}\frac{\partial n'}{\partial E'}dE'\ , \tag{11}$$

or equivalently,

$$\mathscr{A}=2^{3/2}\int_{-1/2}^{n}[E(n,l)-E(n',l)]^{1/2}dn'\ , \tag{12}$$

where the quantum-number dependencies have been explicitly displayed. Differentiating this last equation with respect to $E(n,l)$ gives the first RKR integral

$$f\equiv\frac{r_+-r_-}{2}=2^{-1/2}\int_{-1/2}^{n}[E(n,l)-E(n',l)]^{-1/2}dn'\ . \tag{13}$$

Similarly, by differentiating with respect to λ, it can be shown that the second RKR integral is given by

$$g \equiv \frac{r_-^{-1} - r_+^{-1}}{2}$$
$$= 2^{1/2} \int_{-1/2}^{n} \frac{\partial E(n',l)}{\partial \lambda} [E(n,l) - E(n',l)]^{-1/2} dn' \; . \qquad (14)$$

Thus, after evaluating the f and g integrals the turning points may be obtained from

$$r_\pm = (f/g + f^2)^{1/2} \pm f \qquad (15)$$

as functions of $E(n,l)$.

It is important to recognize that *within the semiclassical formalism, the potential inverted according to this method is unique for a given analytic parametrization of the energy—quantum-number relation.* The f integral fixes the potential function widths that correspond to various values of E, while the g integral provides information concerning how these widths are to be placed with respect to each other. It is somewhat misleading that diatomic RKR curves are usually published as tables of numerical values for a few isolated turning points—those corresponding to the quantum eigenstates. At first glance it seems that a number of continuous functions could be constructed to fit the points. However, one can obtain an RKR curve on as fine an energy or quantum-number mesh as one chooses, and naturally, also as an analytic curve. Because of the semiclassical nature of the RKR method, energies and quantum numbers are regarded as continuous variables. The integrals of Eqs. (13) and (14) would be meaningless otherwise. It is this continuous property of the semiclassical energy that allows an analytic inversion as described here and elsewhere.[3,5]

Let us now examine in more detail the RKR derivation presented above. First, we started out with the assumption of a radial potential. In this case, the quantization condition of Eq. (9) needs to be modified in order to account for the fact that a radial potential is defined on the $(0,\infty)$ semi-infinite interval, while JWKB quantization expects a potential defined on the whole line $(-\infty,\infty)$. This modification is accomplished through the addition of the Langer[6] correction,

$$\Delta V(r) = 1/8r^2 \; , \qquad (16)$$

to the effective potential, i.e.,

$$\Phi(r) \rightarrow V(r) + \lambda/2r^2 + \Delta V(r) \; , \qquad (17)$$

is used when evaluating Eq. (9). Although a Langer-type correction depends on the particular choice of transformation employed to map the $(0,\infty)$ interval into $(-\infty,\infty)$, Eq. (16) is indeed the appropriate correction for the Coulomb-like and radial harmonic-oscillator potentials[5,7] discussed in later sections of this paper. If we adopt Eq. (17) when quantizing the potential, then, for consistency, we need to redefine the area of Eq. (3) by also incorporating the Langer correction into it. Since this amounts to letting $\lambda \rightarrow (l+\frac{1}{2})^2$, the meaning of the relationships of Eqs. (4) and (5) remains the same. The only effect of these changes is that the turning points evaluated according to Eq. (15) no longer correspond to the original effective potential, but rather are the roots of $E = V(r_\pm) + \lambda/r_\pm^2 + \Delta V(r_\pm)$. Therefore, after obtaining a radial potential curve through the RKR method, we must subtract $\Delta V(r)$ in order to obtain the actual effective potential of the system being inverted. This type of correction has been missing from RKR treatments for diatomic molecules. As pointed out previously,[3] when the mass dependence of $\Delta V(r) = \hbar^2/8\mu r^2$ is displayed explicitly (here μ is the reduced mass), it is clear that for the large typical values of μ associated with diatomic molecules this correction is expected to be small and likely to be negligible in most cases. However, $\Delta V(r)$ should be included in problems dealing with low reduced mass systems, e.g., systems with electrons, or the RKR method will result in serious error.

Next, let us elaborate on the origin of the $-\frac{1}{2}$ lower limit in both the f and g integrals. The first appearance of this integral limit is in Eq. (12), where it resulted from a change in integration variable. The right-hand side of Eq. (11) is integrated from V_0, the minimum of the potential well, up to E, as illustrated in Fig. 1(a). If we wish to use n' as the integration variable, the upper limit is easily found as that value of n' which results in an energy E. To find the lower limit we note that at V_0 the turning points coalesce. It follows that the JWKB integral of Eq. (9) vanishes for this situation and leads to $n' + \frac{1}{2} = 0$, which in turn gives $n' = -\frac{1}{2}$ for this limit.

Now we can introduce a semiclassical analog to the Abraham-Moses[1] method. Suppose we wish to delete some of the lower levels, starting from the ground state. The energy eigenvalues, assumed to be analytic functions of n', are then restricted to values of $n' \geq n_0$, where n_0 is a finite and yet to be chosen quantum number. The energy levels with $n' \geq n_0$ are not disturbed. Since we have deleted those energy levels associated with $n' = 0, 1, \ldots, n_0 - 1$, the right-hand side of Eq. (12) must now be integrated from a lower limit of $n_0 - \frac{1}{2}$. Proceeding backwards through the RKR derivation, we see that Eq. (11) still applies, except that V_0 is now replaced with a new minimum value V_{n_0}. Naturally, this leads to a new value for area $\mathscr{A}$. This new area, shown as a shaded region in Fig. 1(b), is bounded by some new distorted effective potential $\Phi(r)$ and the $\Phi(r) = E$ line. The new potential is now forced to satisfy two conditions: (i) It must be such that the modified area of Eqs. (3) and (12) are the same, i.e.,

$$\int_{r_-}^{r_+} [E - \Phi(r)] dr = 2^{3/2} \int_{n_0 - 1/2}^{n} [E(n,l) - E(n'l)]^{1/2} dn' , \qquad (18)$$

and (ii) it must semiclassically reproduce the spectrum for $n \geq n_0$. In other words, it must satisfy the modified quantization condition

$$(n - n_0 + \tfrac{1}{2})\pi = 2^{1/2} \int_{r_-}^{r_+} [E - \Phi(r)]^{1/2} dr \; . \qquad (19)$$

The potential that satisfies these conditions may be obtained by evaluating the following modified version of the RKR equations:

$$f = 2^{-1/2} \int_{n_0 - 1/2}^{n} [E(n,l) - E(n',l)]^{-1/2} dn' \; , \qquad (20)$$

and

$$g=2^{1/2}\int_{n_0-1/2}^{n}\frac{\partial E(n',l)}{\partial\lambda}[E(n,l)-E(n',l)]^{-1/2}dn' \, . \tag{21}$$

If we begin with an energy-level spectrum that is analytic in n and l, Eqs. (20) and (21) will yield a potential that, when semiclassically quantized according to Eq. (19), will reproduce that spectrum, except for the deleted states. Notice that Eq. (19) defines the radial quantum number n_0 as the new ground state. This number will, in general, be larger than zero; nevertheless, the wave function associated with that state will always be nodeless. As an example, let us consider the $n=6$ state of the unmodified model potential. The wave function that characterizes this state will have six nodes, while the unmodified ground state will be nodeless. After deleting the first six levels and forcing the $n=n_0=6$ level to become the new ground state, we find that its wave function has qualitatively collapsed back to the unmodified ground state by losing five nodes. The $n=6$ level, of course, has the same energy in both cases.

If we choose to begin with a semiclassically modified potential, we may add levels to the spectrum by lowering the value of n_0 and thus obtain the other version of the Abraham-Moses algorithm. The addition of extra levels can be carried out only for an already incomplete spectrum, i.e., we cannot add levels when $n_0=0$. Also, the added levels are not arbitrary, they must conform to the analytic expression for $E(n,l)$. Thus, this represents a relatively uninteresting version of the semiclassical algorithm.

A final point that should be stressed here is that the potentials inverted according to this method may be l dependent. There is a pair of f and g integrals for each value of l, and for each pair a corresponding potential function. For the radial-harmonic oscillator treated in the Appendix, we obtain the same modification for all angular momentum values, but for the modified Coulomb potentials examined in Sec. III l dependency is exhibited.

III. MODIFIED COULOMB POTENTIALS

The semiclassical method described in Sec. II requires, as the starting point, a radial model potential with energy levels given by an analytic function of the radial and angular momentum quantum numbers. Two radial model systems that meet these requirements are the radial harmonic oscillator and the Coulomb potential. Other radial potentials that also yield analytic energy levels are actually special cases or simple variations of the two kinds of interaction just mentioned. These variations include the isotonic oscillator[8] or harmonic oscillator with centripetal barrier (HOCB) potential,[9] and the Kratzer[10] or Simons-Finlan[11] oscillator. Thus, it will suffice to present results for only the two generic versions of these radial potentials and the extension to the others will be straightforward. The treatment for the harmonic oscillator resulted in only a trivial upward shift of the potential. Details for this derivation are therefore relegated to the Appendix for completeness. This section, and the rest of the paper, focuses on the more interesting Coulomb model system.

For the cases of an unmodified Coulomb potential (UCP),

$$V_0(r)=-\frac{Z}{r}, \quad 0\le r\le\infty \tag{22}$$

whose energy levels are given by

$$E(n,l)=\frac{-Z^2}{2(n+l+1)^2}, \quad n,l=0,1,2,\ldots , \tag{23}$$

we can readily perform the first modified RKR integral analytically. Here Z is the atomic number. We obtain the result

$$r_+-r_-=-[2\Phi(r_\pm)+Z^2(n_0+l+\tfrac{1}{2})^{-2}]^{1/2} \times(n_0+l+\tfrac{1}{2})/\Phi(r_\pm) \, . \tag{24}$$

Next, we differentiate Eq. (23) with respect to λ,

$$\frac{\partial E(n,l)}{\partial\lambda}=Z^2/(l+\tfrac{1}{2})(n+l+1)^3 \, , \tag{25}$$

and find, from the second modified RKR integral, that

$$\frac{1}{r_-}-\frac{1}{r_+}=2[2\Phi(r_\pm)+Z^2(n_0+l+\tfrac{1}{2})^{-2}]^{1/2}/(l+\tfrac{1}{2}) \, . \tag{26}$$

Then, instead of using Eq. (15) to find expressions for the turning point as functions of n_0, l, and $\Phi(r_\pm)$, we will solve for $\Phi(r_\pm)$ directly. Using Eqs. (24) and (26) to eliminate either one of the turning points we obtain

$$\Phi^2(r_\pm)+[y(l+\tfrac{1}{2}-2y)/r_\pm^2]\Phi(r_\pm) +y^2(l+\tfrac{1}{2})^2/4r_\pm^4-Z^2/r_\pm^2=0 \, , \tag{27}$$

where $y=n_0+l+\frac{1}{2}$. From this quadratic equation we easily obtain

$$\Phi(r_\pm)=\frac{y(2y-l-\frac{1}{2})}{2r_\pm^2}+\frac{sZ}{r_\pm}\left[1+\frac{y^3(y-l-\frac{1}{2})}{Z^2r_\pm^2}\right]^{1/2} , \tag{28}$$

where $s=\pm1$ depending on whether we choose the positive or negative values of the radical. Subsequently, we suppress the subscripts and make us of Eq. (17) to find that

$$V(r)=-\frac{Z}{r}\left[1+\frac{A}{Z^2r^2}\right]^{1/2}+\frac{B}{r^2} \, . \tag{29}$$

The other root to Eq. (27), given by Eq. (28) with $s=+1$, is discarded as unphysical. The two constants in the modified Coulomb potential (MCP) of Eq. (29) are given by

$$A=n_0(n_0+l+\tfrac{1}{2})^3 \tag{30}$$

and

$$B=n_0^2+\tfrac{3}{2}n_0(l+\tfrac{1}{2}) \, . \tag{31}$$

Here we can clearly see that if we let n_0 correspond to the ground state of a Coulomb-type system, the constants A and B vanish and the UCP of Eq. (22) is recovered. As we choose other nonzero n_0 values the potential begins to deviate from Coulombic form although the energy levels with $n\ge n_0$ remain unchanged for a particular value of l.

Once the value of l has been specified the variable of integration can be changed to the principal quantum number N, given by

$$N = n + l + 1 \ . \tag{32}$$

Again, the f and g integrals are done analytically with the results

$$A = (N_0 - l - 1)(N_0 - \tfrac{1}{2})^3 \tag{33}$$

and

$$B = (N_0 - l - 1)(N_0 + l/2 - \tfrac{1}{4}) \ , \tag{34}$$

where N_0 is the lowest value of N chosen and $l < N_0$. In this alternate derivation, use of the quantization condition

$$(N - N_0 + \tfrac{1}{2})\pi = 2^{1/2} \int_{r_-}^{r_+} [E - \Phi(r)]^{1/2} dr \ , \tag{35}$$

was needed for consistency.

Simply by choosing different n_0 or N_0 values along with the appropriate value of l, we can generate a whole family of MCP functions which yield analytic spectra. Table I lists the values of A and B for some of these potentials up to $N_0 = 6$. The first row of this table, included for completeness, corresponds to the unmodified set of Coulomb eigenvalues. In the next two rows we find the values of A and B obtained when we delete the 1s state. For this situation $N_0 = 2$, and consequently l can have values $l = 0$ and $l = 1$. Here we notice that for an UCP with $l = 1$, the 2p state is already the lowest possible level since the repulsive centrifugal term has displaced the effective potential upwards and eliminated the 1s state. Then, it is not surprising that A and B turn out to be zero, i.e., the UCP does not need to be perturbed to delete the 1s state. However, the 2s state, whose energy coincides with that of the 2p state, can also be chosen as our new lowest level. In this $l = 0$ case, there is no centrifugal term to shift the potential upwards and delete the 1s state. Consequently, the A and B constants assume nonzero values in order to make the potential less attractive in just the right way so that the 1s state is eliminated and all the other s states remain unchanged. A similar behavior is found as we scan the A and B columns of Table I for increasing values of N_0.

Let us now consider Fig. 2, where we show a family of modified potentials for $l = 0$ and $Z = 1$. The labels represent the state chosen as the new ground state. We can see in this figure that when no assistance from the centrifugal term is available, the potential must become shallower, i.e., more repulsive as N_0 increases, in order to eliminate more and more levels. Again, we emphasize that none of the highly exited states are modified, we only remove levels from the bottom and proceed upwards.

We can also examine the systematics of these MCP functions from another point of view. Let us choose a value for the lowest principal quantum number allowed, e.g., $N_0 = 6$. This restricts l to a value less than 6; so, we select the 6s, . . . , 6h states as our new ground states. All of these, of course, have the same energy, $E_0 = -Z^2/72$, but result from the different curves associated with each l value. The resulting potentials are plotted in Fig. 3 for $Z = 1$. When we use an $l = 0$, 6s ground-state MCP, we obtain a very shallow (relative to $-1/r$ at intermediate and large radial reparations) potential which when quantized gives E_0 as its lowest eigenvalue. If we let $l = 1$, the MCP obtained is deeper. The corresponding effective potential, when quantized, also results in E_0 as its lowest eigenvalue. As the angular momentum quantum number

TABLE I. Parameters, in atomic units, for the construction of semiclassically modified Coulomb potentials.

N_0	l	Lowest level	A	B	C
1	0	1s	0	0	0
2	0	2s	3.375	1.750	−0.0871
2	1	2p	0	0	0
3	0	3s	31.250	5.500	−0.0902
3	1	3p	15.625	3.250	−0.7028
3	2	3d	0	0	0
4	0	4s	128.625	11.250	−0.0913
4	1	4p	85.750	8.500	−0.7601
4	2	4d	42.875	4.750	−1.7979
4	3	4f	0	0	0
5	0	5s	364.500	19.000	−0.0919
5	1	5p	273.375	15.750	−0.7841
5	2	5d	182.250	11.500	−2.0000
5	3	5f	91.125	6.250	−3.2959
5	4	5g	0	0	0
6	0	6s	831.875	28.750	−0.0922
6	1	6p	665.500	25.000	−0.7973
6	2	6d	499.125	20.250	−2.0911
6	3	6f	332.750	14.500	−3.7414
6	4	6g	166.375	7.750	−5.1486
6	5	6h	0	0	0

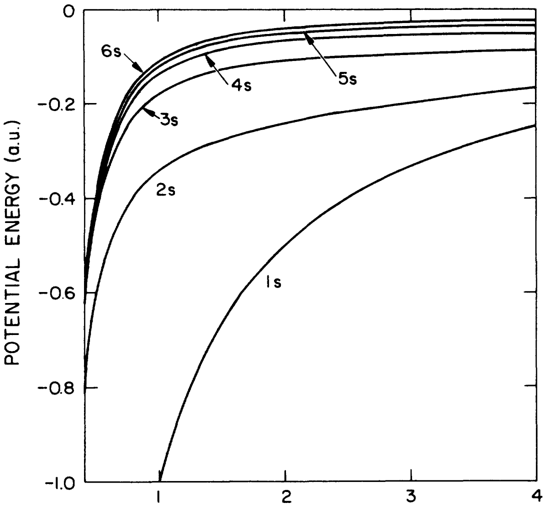

FIG. 2. Modified Coulomb ($Z=1$) potentials with zero angular momentum. The labels indicate the lowest level associated with each curve. The 1*s* curve corresponds to the unmodified $-1/r$ Coulomb potential.

increases and assumes a greater role in making the effective potential more repulsive, the MCP functions become increasingly attractive, even more so than the parent UCP, as can be seen in Fig. 3. Then, when l reaches its highest allowed value $l=5$, the potential collapses back to an UCP since the 6*h* state is already the lowest eigenvalue for $l=5$ and no modification is needed in this case.

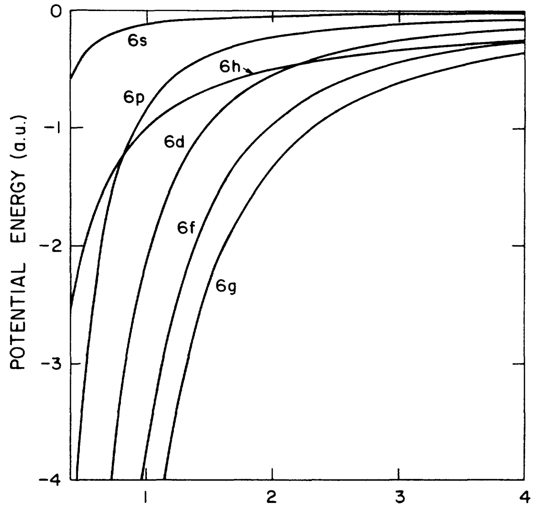

FIG. 3. Family of l-dependent modified Coulomb ($Z=1$) potentials resulting from the removal of all levels with principal quantum number $N<6$. The labels indicate the lowest level associated with each curve. The 6*h* curve coincides with the unmodified $-1/r$ Coulomb potential.

Up to this point we have been studying the qualitative behavior of the MCP functions in the intermediate range of radial distances. Let us now examine the limiting behavior of these functions in their two radial extremes. By inspection of Eq. (29), we may write

$$V(r) \sim (B - A^{1/2})/r^2 = C/r^2 \tag{36}$$

for small radial separations. This implies that all the MCP functions are much more attractive than their parent UCP at short range since $C=B-A^{1/2}$ is always less than zero, except, of course, when $l=N_0-1$ and both A and B vanish. In addition, an interesting observation is that this limiting behavior is independent of Z, which is a measure of the strength of the Coulomb interaction. Values of C are given in the last column of Table I. From these data we conclude that at short range the ordering of the curves in Fig. 2 will reverse. In Fig. 3, the 6*s* curve will eventually become deeper than the 6*h* curve as r becomes small and the ordering will be 6*h*, 6*s*, 6*p*, 6*d*, 6*f*, and 6*g*, with the 6*g* MCP as the most attractive function.

For large radial separations we have

$$V(r) \sim -\frac{Z}{r} + \frac{B}{r^2} - \frac{A}{2Zr^3} + \frac{A^2}{8Z^3r^5} + \cdots , \tag{37}$$

which is basically a Coulomb potential with small perturbations; after the $1/r^2$ term these perturbations have only odd powers of $1/r$. In this limit the ordering shown in Figs. 2 and 3 will be preserved, with the exception of the 6*h* curve in Fig. 3. This curve is purely Coulombic in nature and will eventually become the deepest potential. Finally, two other general features of these MCP functions are that they are always negative and monotonic; they exhibit no barriers or local minima. In practical applications, the potential to be quantized takes the form

$$U(r) = V(r) + \lambda/2r^2 . \tag{38}$$

Since $V(r)$ is l dependent, it is perhaps more appropriate to incorporate the centrifugal part into it and write

$$U(r) \equiv U_l(r) = -\frac{Z}{r}\left[1 + \frac{A_l}{Z^2r^2}\right]^{1/2} + \frac{B_l}{r^2} \tag{39}$$

for the effective potential that is actually used in a calculation. Here $A_l = A$, and

$$\begin{aligned} B_l &= n_0^2 + \tfrac{3}{2} n_0 (l + \tfrac{1}{2}) + l(l+1)/2 \\ &= (N_0 - l - 1)(N_0 + l/2 - \tfrac{1}{4}) + l(l+1)/2 . \end{aligned} \tag{40}$$

Some values of B_l are given in Table II. Viewed from this perspective, the MCP functions may now possess infinite repulsive barriers at short range, depending on whether the constant $C_l = B_l - A_l^{1/2}$ in

$$U_l(r \ll 1) \sim C_l/r^2 \tag{41}$$

is positive or negative. For cases with an infinite barrier or hard wall ($C_l > 0$), we may define the barrier location r_0 as the r value that satisfies

$$U_l(r) = 0 . \tag{42}$$

This barrier location is given by

$$r_0 = (B_l^2 - A_l)^{1/2} Z . \tag{43}$$

If an infinite positive barrier exists, then there is also a

TABLE II. Parameters, in atomic units, for the construction of semiclassically modified effective Coulomb potentials.

N	l	Lowest level	B_l	C_l	Zr_0	Zr_m
1	0	1*s*	0	0		
2	0	2*s*	1.750	−0.0871		
2	1	2*p*	1.000	1.0000	1.0000	2.0000
3	0	3*s*	5.500	−0.0902		
3	1	3*p*	4.250	0.1726	1.5612	4.2597
3	2	3*d*	3.000	3.0000	3.0000	6.0000
4	0	4*s*	11.250	−0.0913		
4	1	4*p*	9.500	0.2399	2.1213	7.0217
4	2	4*d*	7.750	1.2021	4.1458	9.9315
4	3	4*f*	6.000	6.0000	6.0000	12.0000
5	0	5*s*	19.000	−0.0919		
5	1	5*p*	16.750	0.2159	2.6810	10.2073
5	2	5*d*	14.500	1.0000	5.2915	14.4725
5	3	5*f*	12.250	2.7041	7.6771	17.4918
5	4	5*g*	10.000	10.0000	10.0000	20.0000
6	0	6*s*	28.750	−0.0922		
6	1	6*p*	26.000	0.2027	3.2404	13.7659
6	2	6*d*	23.250	0.9098	6.4372	19.5501
6	3	6*f*	20.500	2.2586	9.3541	23.6330
6	4	6*g*	17.750	4.8514	12.1937	27.0232
6	5	6*h*	15.000	15.0000	15.0000	30.0000

minimum in the potential. The location r_m of this minimum is found from

$$\left.\frac{dU_l(r)}{dr}\right|_{r_m}=0\ . \tag{44}$$

From Eq. (39) we immediately find that

$$\begin{aligned} r_m &= 2^{1/2}[(B_l^2-A_l)+B_l(B_l^2-A_l)^{1/2}]^{1/2}/Z \\ &= 2^{1/2}(r_0^2+B_l r_0/Z)^{1/2}\ . \end{aligned} \tag{45}$$

Values of the parameters C_l, r_0, and r_m are also cited in Table II for $Z=1$. The C_l values indicate that except for those functions with *s* states as ground states, all MCP functions possess an infinite repulsive wall at short range.

Finally, before concluding this section, we compare the present semiclassical result with that reported by Abraham and Moses[1] for the hydrogen atom. Expressing our potential in the form of Eq. (1) for $Z=1$, $N_0=2$, and $l=0$, we can write

$$V'_{\rm sc}(r)=[1-(1+3.375/r^2)^{1/2}]/r+1.75/r^2\ . \tag{46}$$

The quantal result of Abraham and Moses[1] is given by

$$V'_q(r)=8r(r+1)/(2r^2+2r+1)^2\ . \tag{47}$$

The sc and q subscripts denote the semiclassical or quantal nature of the result. These two modifications are compared in Fig. 4(a). Qualitatively, both methods agree in that in order to delete the 1*s* state we must set up a barrier. However, the details of the shape of the barrier differ considerably. The quantal barrier approaches zero in the limit of vanishing r, while the semiclassical barrier changes sign at some small value of r and behaves as $-0.087/r^2$ asymptotically in the same limit. In the other extreme, i.e., large-r values, Eqs. (46) and (47) both decay as β/r^2, but with different β coefficients, 1.75 and 2, respectively.

It is probably more instructive to compare the actual potentials themselves and not just the modifications. Figure 4(b) shows plots of the MCP functions obtained through both methods. An interesting situation becomes apparent: the two potentials of Fig. 4(b) differ considerably and yet both of them give rise to the same energy spectrum. As a check, the semiclassical MCP functions were numerically quantized, resulting in energy levels that reproduced the exact spectrum with an accuracy better than 5×10^{-5} a.u. Typical results are shown in Table III. Since the deviations are partly due to the numerical scheme (Numerov integration) itself, this kind of agreement suggests that it may be possible to quantize the potential of Eq. (39) analytically from a quantal point of view. Such a quantization is clearly exact when done semiclassically. The reason for the MCP "degeneracy" mentioned above is not entirely clear. It may be simply attributed to the different quantal or semiclassical nature or we might postulate the existence of a number, perhaps infinite, of different families of potentials that share the same (incomplete) energy spectra. One such family has been presented here. It would be of interest, although out-

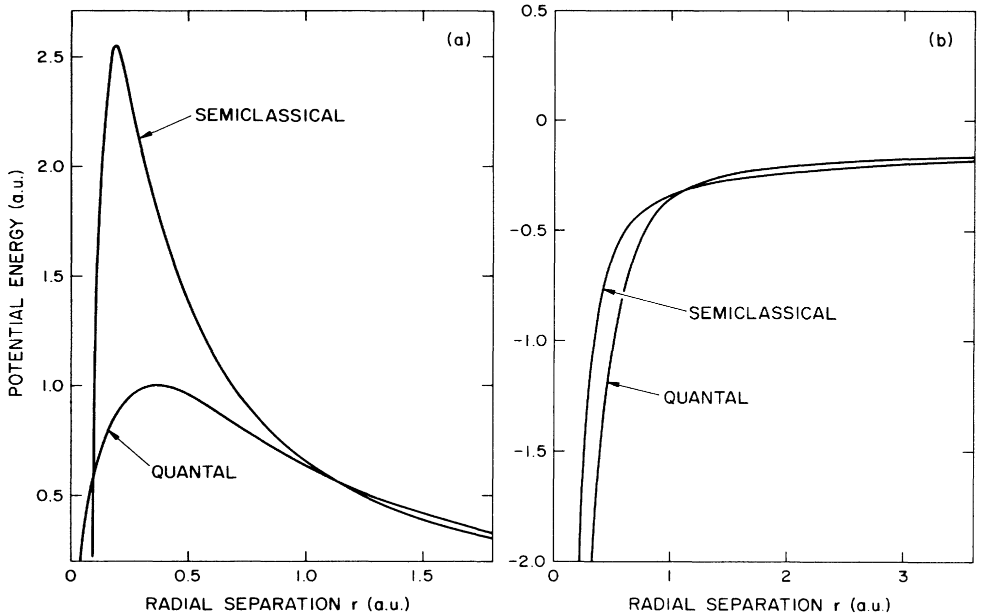

FIG. 4. Comparison between quantal and semiclassical (a) modifications and (b) potential functions resulting from the removal of the 1*s* state of the hydrogen atom.

side the scope of the present work, to explore the MCP family resulting from the quantal version of the method. Unfortunately, the modifications, derived one at a time, contain integrals that become progressively more difficult; this hinders a systematic study.

IV. SUMMARY AND CONCLUDING REMARKS

A simple semiclassical method for generating radial potential functions with eigenvalues given by exact analytic expressions has been presented. Application of this method to the Coulomb potential has been discussed in detail. The resulting MCP functions are given by simple l-dependent formulas. A property of these modified potentials is that when levels are removed from the spectrum, nodes are also removed from the wave functions of the states whose energy levels are not perturbed. Thus, it turns out that every "new" ground state ($n = n_0$ or $N = N_0$) is nodeless, i.e., it qualitatively resembles the "original" ground state ($n = 0$ or $N = 1$).

Another property of the MCP functions is that in order to eliminate some of the states, the modification to the Coulomb potential takes the shape of a potential barrier. This MCP feature is very reminiscent of the pseudopotential method[12] for modeling valence electron-atomic core interactions. A pseudopotential is basically a Coulomb-type potential into which a barrier has been incorporated for the purpose of simulating the Pauli exclusion principle and other outer-electron—atomic-core interactions. This barrier prevents the valence electrons from entering the core. In the case of a system with a single valence electron, e.g., an alkali-metal atom, the Pauli principle modifies the hydrogenlike set of levels as follows: for a given l, some of the allowed ($N \geq l+1$) values of the principal quantum number are effectively eliminated. For example, in the Cs atom the lowest $l = 0$ state allowed is the 6*s* state. Any other *s* states with a lower N are Pauli forbidden. If there were no other perturbations to the energy levels, it appears that either the quantal or the semiclassi-

TABLE III. Numerically quantized binding energies, in atomic units, for the first ten states of the $Z = 1$ family of modified Coulomb potentials resulting from the removal of all levels with principal quantum number $N < 6$. Exact values are given by $E = -1/2N^2$.

N	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
6	0.013 916	0.013 927	0.013 935	0.013 921	0.013 901	0.013 889
7	0.010 208	0.010 230	0.010 226	0.010 221	0.010 214	0.010 204
8	0.007 813	0.007 826	0.007 825	0.007 823	0.007 819	0.007 813
9	0.006 171	0.006 181	0.006 181	0.006 179	0.006 177	0.006 173
10	0.005 000	0.005 006	0.005 005	0.005 005	0.005 003	0.005 000
11	0.004 132	0.004 136	0.004 136	0.004 136	0.004 134	0.004 132
12	0.003 472	0.003 475	0.003 475	0.003 475	0.003 474	0.003 472
13	0.002 958	0.002 960	0.002 961	0.002 960	0.002 960	0.002 959
14	0.002 551	0.002 553	0.002 553	0.002 552	0.002 552	0.002 551
15	0.002 222	0.002 224	0.002 224	0.002 223	0.002 223	0.002 222

cal MCP functions would be the logical candidates for the analytic modeling of the exclusion principle in systems with one valence electron. Naturally, matters are complicated by other effects that further perturb this truncated set of hydrogenic energy levels. The largest of these is the core-induced phase shift, relative to the Coulomb shift, of the valence wave function in the core region. The corresponding modification of the energy levels is a systematic correction or quantum defect[13] that shifts the value of the principal quantum number in the hydrogenic level formula. The combination of these two types of perturbation leads to an energy-level formula given by

$$E=-\frac{Z^2}{2(N-\delta)^2},\quad N\geq N_0 \tag{48}$$

where δ is the quantum defect and N_0 is the lowest value of N allowed by the exclusion principle. As far as the energy levels are concerned, the quantum defect attempts to counteract the restriction of the exclusion principle by lowering N to some smaller effective quantum number. Although it is not entirely clear how closely coupled these two types of modification are, it is reasonable to suggest that the MCP functions may be useful as first-order approximations in the analytic characterization of the Pauli principle. If that were the case, the MCP could be employed as the starting point of more detailed modeling of hydrogenlike atomic systems.

ACKNOWLEDGMENT

The National Center for Atmospheric Research is sponsored by the National Science Foundation.

APPENDIX: MODIFIED RADIAL-HARMONIC OSCILLATORS

We begin with a radial model potential of the form

$$V_0(r)=\frac{\omega^2}{2}r^2,\quad 0\leq r\leq\infty \tag{A1}$$

where ω is the angular frequency. The corresponding energy spectrum is given by

$$E(n,l)=\omega(2n+l+\tfrac{3}{2}),\quad n,l=0,1,2,\ldots . \tag{A2}$$

With this expression for the energy levels, it is straightforward to evaluate the f integral of Eq. (20). We find a width given by

$$r_+-r_-=(2^{1/2}/\omega)[\Phi(r_\pm)-\omega(2n_0+l+\tfrac{1}{2})]^{1/2} . \tag{A3}$$

The g integral of Eq. (21) is similarly evaluated. We obtain

$$\frac{1}{r_-}-\frac{1}{r_+}=[2^{1/2}/(l+\tfrac{1}{2})][\Phi(r_\pm)-\omega(2n_0+l+\tfrac{1}{2})]^{1/2} , \tag{A4}$$

where we have used the result

$$\frac{\partial E(n,l)}{\partial\lambda}=\frac{\omega}{2l+1} . \tag{A5}$$

From Eqs. (A3) and (A4), it follows that

$$\Phi(r_\pm)=\frac{\omega^2}{2}r_\pm^2+\frac{(l+\frac{1}{2})^2}{2r_\pm^2}+2n_0\omega . \tag{A6}$$

Therefore, the Langer-corrected family of modified potentials has the form

$$V(r)=\frac{\omega^2}{2}r^2+2n_0\omega,\quad n_0=0,1,2,\ldots \tag{A7}$$

which is simply the original model potential shifted by an integral multiple of the level spacing 2ω. This shift adds nothing new since we can always add a constant to a potential function with the result that the energy levels are also shifted by the amount. However, this example shows that the semiclassically derived modified potentials are not always l dependent. Finally, it may be pointed out that for this particular model potential we can apply the other version of the algorithm, the addition of extra levels, with no restrictions. To add levels we simply shift the potential downward by an integral multiple of the level spacing, increasing the allowed values of n_0 to 0, ± 1, ± 2, etc. The fact that $n > n_0$ may be negative does not mean that the effective quantum numbers are allowed to become negative. The modified radial quantum number, and therefore the number of nodes in the corresponding wave function, is actually $n-n_0$, as shown in Eq. (19). In other words, the modification amounts to a mapping of n into $n-n_0$, a quantity that always has zero as its lowest integer value.

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