Eigenvalue Method

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The eigenvalues, E_{nl}, of the radial Schrödinger equation are approximated by $c_k(E=E_{nl}) = 0$ ($k = 2, 3, \ldots \infty$), where E is the energy and the c_k are the power-series coefficients of $f(r) = \psi(r)/[r^{l+1}w(r)]$ with $\psi(r)$ the wave function and $w(r)$ a weight function. This is an extension of the method used to solve certain potentials exactly where $c_k(E=E_{nl}) = 0$ terminates a power series.

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The radial Schrödinger equation can be solved exactly for certain potentials[1] such as the harmonic oscillator or Coulomb potential by writing the wave function in the form

$$\psi(r) = w(r)r^{l+1}\sum_{k=1} c_k(E)r^{k-1}, \tag{1}$$

with E the energy, and determining the eigenvalues E_n ($n = 1, 2, \ldots$) by the condition $c_k(E=E_n) = 0$ (for appropriate values of k and n) which terminates the power series. In this Letter I extend this method to potentials in the radial Schrödinger equation which cannot be solved exactly. I express their wave functions in the form of Eq. (1) and approximate E_n by the $E_n^{(k)}$ ($k = 2, 3, 4, \ldots$) which are defined by the condition $c_k(E=E_n^{(k)}) = 0$ with $E_i^{(k)} > E_j^{(k)}$ for $i > j$. While I have no proof that $E_n^{(k)} \to E_n$ as $k \to \infty$ I do offer an argument concerning the validity of approximating E_n by $E_n^{(k)}$ for a large class of potentials for certain choices of $w(r)$ in (1) and I give numerical evidence of convergence for several nonlinear potentials. Approximation of the eigenvalues by means of $c_k(E) = 0$ is simple in concept and in computation. For many potentials obtaining $c_k(E)$ (from a recurrence relation) and solving $c_k(E) = 0$ requires far fewer computational steps than standard methods such as matrix diagonalization,[2] the Hill determinant,[3] variational procedures,[4] or other power-series methods[5,6] do at their kth order. These other power-series methods are the closest in approach to the present work although they do not consider what the square integrability of $\psi(r)$ means in terms of the behavior of $c_k(E)$.

Let us consider the radial Schrödinger equation

$$H_l\psi(r) = E\psi(r), \tag{2}$$

$$H_l = -\tfrac{1}{2}(d^2/dr^2) + l(l+1)/2r^2 + V(r) \tag{3}$$

for $0 \leq r \leq \infty$ where $l(l+1) \geq 0$ and $\psi(r)$ denotes the solution of (2), for arbitrary real E, which behaves as r^{l+1} as $r \to 0$. If ψ is square integrable then $\psi = \psi_n$ and $E = E_n = E_{nl}$ (i.e., l is understood) otherwise $\psi = \psi_c$ and $E = E_c$. The weight function $w(r)$ will be designated as a member of class W if $w(r)$ and $f(r) = \psi/r^{l+1}w(r)$ are in one of the following four categories: (1) $w(r) = \exp(-\alpha r)$, $\alpha > 0$. (2) $w(r) = \exp(-\alpha r^2)$, $\alpha > 0$; $f(-r) = \pm f(r)$. (3) $w^{-1}(z)$, for complex z, is analytic for $0 \leq z < \infty$; and there exists an $\alpha > 0$ for which $\psi e^{-\alpha r}/w(r)$ is square integrable if and only if $E = E_n$. (4) $w^{-1}(z)$ is analytic for $0 \leq z < \infty$; $f(-r) = \pm f(r)$; and there exists an $\alpha > 0$ for which $\psi\exp(-\alpha r^2)/w(r)$ is square integrable if and only if $E = E_n$. The first category is useful when $V(r) \to 0$ as $r \to \infty$; the second for perturbations of harmonic oscillators with $V(-r) = \pm V(r)$; the third and fourth allow for a choice of other $w(r)$'s for nonlinear potentials with and without symmetry. For most potentials of interest,[7] $\psi_n \sim e^{-S}$ and $\psi_c \sim e^{+S}$ as $r \to \infty$ with $S \sim \beta r^\mu$ ($\beta > 0$, $\mu \geq 1$) so that it is usually not difficult to find a range of $w(r)$'s whose asymptotic behavior is sufficiently close to that of ψ_n to satisfy either category 3 or 4. Categories 1 and 2 have been used previously by Killingbeck,[6] in an improvement of the method of Secrest, Cashion, and Hirschfelder.[5]

I now show that if $w(r)$ is in class W and $zV(z)$ is analytic for $0 \leq z < \infty$ then

$$\lim_{k\to\infty} A_k c_k(E) = 0 \quad \text{if } E = E_n,$$
$$= \infty \quad \text{if } E = E_c, \tag{4}$$

where $A_k = p\Gamma(q+1)/\alpha^q > 0$, $\Gamma(q+1)$ is the gamma function, $q = q(k) = (k+\gamma+l)/p$, $\alpha > 0$ is defined in the description of class W, $\gamma > 0$ is to be defined, and $p = 1$ ($p = 2$) for $w(r)$ in categories 1 or 3 (2 or 4). Equation (4) serves as our basis for approximating the E_n by the roots of $A_k c_k(E) = 0$ ($k = 2, 3, 4, \ldots$). These roots are the $E_n^{(k)}$ since $A_k > 0$. The above conditions on $V(r)$ and $w(r)$ imply that ψ can be written in the form of Eq. (1) with the series uniformly convergent. Since ψ_n is square integrable and ψ_c is not there exists a $\gamma > 0$ such that $r^\gamma\psi_n \to 0$ as $r \to \infty$ but $r^\gamma\psi_c \to \infty$ as

$r \to \infty$ [this can also be seen from an asymptotic analysis[7] of Eq. (2)]. Let $F(r,E) = r^{\gamma}\psi$; then the eigenvalues E_n are uniquely determined as those E for which $F(\infty, E) = 0$. Since $F(0,E) = 0$,

$$F(\infty, E) = \int_0^{\infty} g(r)dr, \tag{5}$$

where

$$g(r) = d(r^{\gamma}\psi)/dr \tag{6}$$

with the integral in (5) infinite if $E = E_c$. We first consider $w(r)$ in categories 1 and 2 of class W; then placing Eq. (1) with $w(r) = \exp(-\alpha r^p)$ ($p = 1$ or 2) in Eq. (6) gives

$$g(r) = \exp(-\alpha r^p) \sum_{k=1}^{\infty} b_k r^{k+\gamma+l-1}, \tag{7}$$

where

$$b_k = pqc_k - \alpha p c_{k-p} \tag{8}$$

with $q = q(k)$ and $c_{k-p} = 0$ if $k - p \le 0$. Since the series in (7) is uniformly convergent for $0 \le r < \infty$ we can place (7) in (5) and carry out a term-by-term integration to find

$$F(\infty, E) = \lim_{k\to\infty} F_k(E), \tag{9}$$

$$F_k(E) = \sum_{j=1}^{k} pqc_j \Gamma(q)/\alpha^q - \sum_{j=1}^{k} \alpha p c_{j-p}\Gamma(q)/\alpha^q, \tag{10}$$

where $q = q(j)$. Making the change of index $j \to j + p$ in the second sum in (10) and subtracting it from the first sum, one finds (for $p = 1$, or $p = 2$ with either all the c_{2j}'s zero or all c_{2j+1}'s zero) that $F_k(E)$ is given by $A_k c_k(E)$. This establishes Eq. (4) for $w(r)$ in categories 1 and 2. For $w(r)$ in category 3, we let $\psi = w(r)e^{\alpha r}\psi_1$, $\psi_1 = r^{l+1}e^{-\alpha r} \times f(r)$, and hence $\psi = r^{l+1}w(r)f(r)$. For $w(r)$ in category 4, we let $\psi = w(r)\exp(\alpha r^2)\psi_2$, $\psi_2 = r^{l+1} \times\exp(-\alpha r^2)f(r)$, and hence $\psi = r^{l+1}w(r)f(r)$. Since $f(r)$ then has a convergent power series [$w^{-1}(z)$ is analytic for $0 \le z < \infty$] and in categories 3 and 4, ψ_1 and ψ_2, respectively, are square integrable if and only if $E = E_n$, we can treat ψ_1 as a ψ with a $w(r)$ in category 1 and ψ_2 as a ψ with a $w(r)$ in category 2. Hence Eq. (4) holds for $w(r)$ in class W.

The fact that $A_k c_k(E_c) \to \infty$ as $k \to \infty$ while $A_k c_k(E_n) \to 0$ leads us to an intuitive expectation (but not a proof) that for sufficiently large k, for a given $M > 0$, those E_c for which $|A_k c_k(E_c)| < M$ will be good approximations to an E_n. Thus $E_n^{(k)}$, which satisfies $A_k c_k(E_n^{(k)}) = 0$, should for sufficiently large k be a good approximation to E_n which satisfies $A_k c_k(E_n) = \epsilon_k$ with $|\epsilon_k| \to 0$ as $k \to \infty$. This appears to be the case for the potentials considered in Tables I and II. In the first two columns of Table I, I consider $V(r) = r^2/2 + \lambda r^4$ using $w(r) = \exp(-\nu r^2)/2$ which does not have

TABLE I. Eigenvalues, E_{nl}, from $c_k(E_{nl}) = 0$ where $\psi(r) = w(r)r^{l+1}\sum c_k r^{2k-2}$. (1D, one-dimensional.)

k \ $V(r)$; n, l; $w(r)$	$r^2/2 + 10r^4$; $n = 1$, 1D; $\exp(-\nu r^2)/2$, $\nu = 9/2$	$r^2/2 + r^4/2$; $n = 4$, $l = 2$; $\exp(-\nu r^2)/2$, $\nu = 9/2$	$r^4 + r^6/10$; $n = 7$, 1D; $\exp(-ar^2 - br^4)$, $a^2 = 5/4$, $b^{-2} = 80$
4	1.312 604 006 513	21.483 014 640 05	
8	1.491 168 507 807	20.648 022 238 24	
12	1.504 567 305 039	23.320 408 010 66	18.434 457 754 55
16	1.505 137 941 860	23.385 267 973 38	18.273 579 016 99
20	1.505 020 775 435	23.289 916 481 31	18.264 976 481 23
24	1.504 978 504 628	23.294 552 579 60	18.264 372 518 79
28	1.504 972 063 514	23.294 736 979 38	18.264 322 430 69
32	1.504 972 088 588	23.294 733 442 50	18.264 317 639 77
36	1.504 972 357 330	23.294 733 045 53	18.264 317 121 15
40	1.504 972 413 832	23.294 733 031 88	18.264 317 058 63
44	1.504 972 411 757	23.294 733 031 71	18.264 317 050 34
48	1.504 972 408 158	23.294 733 031 73	18.264 327 049 15
52	1.504 972 407 589	23.294 733 031 73	18.264 317 048 97
56	1.504 972 407 719	23.294 733 031 73	18.264 317 048 94
60	1.504 972 407 783	23.294 733 031 73	18.264 317 048 93
∞	1.504 972 407 785	23.294 733 031 73	18.264 317 048 93

TABLE II. Eigenvalues, E_{nl}, from $c_k(E_{nl}) = 0$ where $\psi(r) = \exp[-(-2E)^{1/2}r]r^{l+1} \times \sum c_k r^{k-1}$.

k \ $V(r)$; n, l	$-1/r + r/20$; $n=1, l=0$	$-r^{-1}\exp(-0.15r)$; $n=1, l=0$	$-\exp(-r/20)$; $n=1, l=1$
4	− 0.386 539 789 364 9	− 0.381 950 451 432 9	
8	− 0.427 557 360 311 5	− 0.365 619 525 913 3	− 0.653 601 107 703 9
12	− 0.428 111 157 062 8	− 0.365 463 624 547 2	− 0.670 505 265 469 2
16	− 0.428 119 953 095 3	− 0.365 460 899 680 7	− 0.670 311 305 406 6
20	− 0.428 119 980 722 9	− 0.365 460 806 201 7	− 0.670 290 666 990 8
24	− 0.428 119 973 443 9	− 0.365 460 800 568 2	− 0.670 289 562 653 9
28	− 0.428 119 973 015 8	− 0.365 460 800 023 7	− 0.670 289 449 228 9
32	− 0.428 119 973 005 7	− 0.365 460 799 945 2	− 0.670 289 497 087 0
36	− 0.428 119 973 006 2	− 0.365 460 799 929 3	− 0.670 289 497 413 2
40	− 0.428 119 973 006 3	− 0.365 460 799 925 0	− 0.670 289 497 481 1
∞	− 0.428 119 973 006 3	− 0.365 460 799 923 1	− 0.670 289 497 480 6

the same asymptotic behavior as ψ_n as $r \to \infty$. The parameter ν is a function of the anharmonicity and state chosen to improve the rate of convergence. As an example of estimating ν, I consider the ground state of $V(r) = r^2/2 + \lambda r^4$ in one dimension ($l = -1$) and determine ν by $\nu = 2E_1$ where E_1 is given by $c_4(E_1) = 0$. This gives the equation for ν:

$$\nu^3 - \nu - 3\lambda = 0. \quad (11)$$

Solving (11) and using $E_1 = \nu/2$ one finds as $\lambda \to 0$, $E_1 = \frac{1}{2} + 3\lambda/4 + O(\lambda^2)$, the first-order perturbation theory result; and for $\lambda \to \infty$, $E_1 \sim 0.72\lambda^{1/3}$ compared with the known asymptotic behavior,[5] $E_1 \sim 0.67\lambda^{1/3}$. At higher orders one can continue to let ν depend explicitly on E or, having determined a value for ν (such as $\nu = \frac{9}{2}$ in Table I), retain it for each other. In the third column of Table I, a $w(r)$ (in category 3) with the correct asymptotic behavior is used for $V(r) = r^4 + r^6$. The sixtieth-order calculation for these potentials required approximately the same computer time as obtaining one root of a 15×15 matrix. In Table II, I consider $V(r) = -1/r + \lambda r$, a Yukawa potential, and an exponential potential, using a weight function, $w(r) = \exp[-(-2E)^{1/2}r]$, which depends explicitly on E. This gives the correct asymptotic behavior for the last two of these potentials which have infinite power series. The fortieth-order calculation for these two potentials in Table II required approximately twice the computer time of the sixtieth-order calculations in Table I since the number of terms in their recurrence relation for c_k increases with k, unlike a finite polynomial potential for which the number of terms is fixed. Applications of this method to other potentials of interest will be given elsewhere.

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