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Note

The Canonical Functions Method and Singular Potentials

The numerical integration of the radial Schrödinger equation

$$d^2y/dr^2 + (E - U(r) - l(l+1)/r^2)\, y(r) = 0 \tag{1}$$

requires a special attention when the potential $U(r)$ is singular at the origin (l is a nonnegative integer; E is the energy).

Two recent papers by Buendia and Guardiola [1] and Ixaru [2] considered potentials of the form

$$U(r) = a(r)/r + b(r), \tag{2}$$

where $a(r)$ and $b(r)$ are "well-behaved" functions. This function U illustrates a class of potentials of interest for many problems in physics. The two works [1–2] mainly try to determine the energy E when the wave function $y(r)$ obeys the boundary conditions

$$y(0) = 0 \tag{3a}$$

$$y(r) \xrightarrow[r \to \infty]{} 0. \tag{3b}$$

For this eigenvalue problem, the conventional Cooley shooting method [3] using the Numerov integrator [4]

$$y_{n+1} - 2y_n + y_{n-1} = \frac{h^2}{12}(y''_{n+1} + 10y''_n + y''_{n-1}) \tag{4}$$

is not applicable in the usual way, since $y''_i = (V_i - E)\, y_i$ at a point r_i with $V = U + l(l+1)/r^2$) cannot be evaluated in the vicinity of $r_i = 0$. The authors of [1–2] start the integration at a large value R of r and integrate Eq. (1) backwards till $r = 0$, where $y_0 = y(0)$ must be equated to zero in order to deduce the eigenvalue E.

By using Eq. (4), y is given as

$$y_0 - 2y_1 + y_2 = \frac{h^2}{12}(y''_0 + 10y''_1 + y''_2),$$

where y''_0 involves $V(0)$ which is infinite. The authors of [1–2] tried to approximate y''_0 by appropriate functions of the form

$$y''_0 \sim f(y_1, y_2, y''_1, y''_2)$$

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and to eliminate the undesirable use of $V(0)$. This difficulty is not eliminated when one replaces the Numerov integrator by other well-known integrators.

The aim of this note is to show that the "canonical functions method" [5] is a powerful alternative to the treatment outlined above. In this method the computation of the wavefunction $y(r)$ (implying an initial value problem) is replaced by that of the canonical functions $\alpha(r_0; r)$ and $\beta(r_0; r)$ which are particular solutions of Eq. (1) with the initial values

$$\alpha(r_0; r_0) = 1, \qquad \alpha'(r_0; r_0) = 0 \tag{5a}$$

$$\beta(r_0; r_0) = 0, \qquad \beta'(r_0; r_0) = 1, \tag{5b}$$

r_0 being an "arbitrary" origin, $0 < r_0 < \infty$.

The use of α and β allows

(i) the determination of the initial values $y(r_0)$ and $y'(r_0)$, by using the relation

$$y(r) = y(r_0)\,\alpha(r_0; r) + y'(r_0)\,\beta(r_0; r) \tag{6}$$

and, by imposing the boundary condition (3a), we find

$$y'(r_0)/y(r_0) = \lim_{r \to 0} -\alpha(r_0; r)/\beta(r_0; r);$$

or, by imposing the boundary condition (3b), we find

$$y'(r_0)/y(r_0) = \lim_{r \to \infty} -\alpha(r_0; r)/\beta(r_0; r).$$

(ii) The determination of the eigenvalue E, since one may consider the function

$$q(r) = -\alpha(r_0; r)/\beta(r_0; r) \tag{7}$$

and the two limits

$$q^+ = \lim_{r \to \infty} q(r) \tag{8a}$$

$$q^- = \lim_{r \to 0} q(r) \tag{8b}$$

and may impose the continuity condition for y'/y at r_0,

$$q^+ = q^-. \tag{9}$$

This equation is fulfilled only when E is an eigenvalue [5].

For the present problem, the main advantage of the canonical functions method, outlined above, lies in the fact that the limit q^- is reached for $r \gtrsim 0$, and that the use of $V(0)$ is simply avoided. This advantage is already shown in a previous work [6], where we used the Lennard–Jones function $U(r) = \text{const} \times (1/r^{12} - 1/r^6)$.

To show the validity of the present method, we consider the Coulomb potential $U(r) = -2/r$ used in [1–2] having the exact eigenvalues $E = -1/(l+1)^2$.

The numerical application for this potential is in every aspect similar to that of the Morse potential used in [5]. It can be summarized as follows.

For an arbitrary value of the "parameter" E ($E < 0$), the canonical functions α and β ar computed for $r \geqslant r_0$: by using a convenient integrator, Eq. (1) is integrated starting at r_0 for α and β simultaneously with the initial values defined in (5). We move on towards large values of r; this integration is stopped when the function $q(r) = -\alpha/\beta$ reaches a constant limit $q^+(E)$, within the computer precision, for a value of r that we call R.

This integration, repeated for $r \leqslant r_0$, allows the determination of $q^-(E)$ obtained at a value r_s of r.

The eigenvalue problem is then reduced to consider the "eigenvalue function" [5] $F(E) = q^+(E) - q^-(E)$ for $E < 0$, and to look to the zeros of this function when the parameter E varies between 0 and $-\infty$. These zeros are nothing but the eigenvalues related to the given potential.

Numerically, this treatment is quite simple. The behavior of α and β illustrated in [5] shows that the two asymptotes of $q(r)$ are reached for $V(r) \lesssim E$, where the exponential growth of α and β is not so dominant as to present a numerical problem. On the other hand, the function $F(E)$ behaves like $\tan(aE + b)$ (a and b are constants) [5], and the determination of its zeros is done by conventional procedures.

In Table I we give the eigenvalues E^{PM} computed by the present method (PM) for several values of l ($l = 5$, 10, 15, 20, 25). We give for each value of l the value R of r for which the function $q(r)$ reaches its limit q^+ (within the computer

TABLE I

Eigenvalues E^{PM} Computed by the Present Method (PM) with the KVS Integrator for Several Values of l and Compared to the Exact Values E^c for the Coulomb Potential

l	E^{PM}	E^c	r_0	r_s	R
5	−0.027777778	−0.02777778	30	1.5	164
10	−0.0082644628	−0.0082644628	110	14	416
15	−0.0039062500	−0.00390625	240	48	698
20	−0.0022675737	−0.0022675737	420	113	1,084
25	−0.0014792899	−0.0014792899	650	201	1,622

Note. For each l the starting point r_0 and the obtained limit points r_s (~ 0) and R ($\sim \infty$) are given in the last columns. (All values in a.u.)

TABLE II

Variation of the Function $q(r)$ versus r for $l=5$ ($E=-0.027777778$)

$r<r_0$		$r>r_0$	
r	$q(r)$	r	$q(r)$
30	—	30	—
23.112	0.13274413	36.888	−0.13253878
17.961	0.063573543	45.553	0.036529527
14.076	0.042279341	56.495	0.0059220642
11.120	0.035491174	70.360	0.027814441
8.852	0.033761658	87.998	0.033027094
7.098	0.033407583	110.825	0.033330502
5.730	0.033345191	130.163	0.033333300
4.656	0.033335144	147.796	0.033333333
3.806	0.033333604	163.863	0.033333333
3.129	0.033333374		
2.587	0.033333339		
2.149	0.033333334		
1.795	0.033333333		
1.516	0.033333333		

Note. The values of $q(r)$ are given for $r \leqslant r_0$ then for $r \geqslant r_0$.[a] The theoretical value q^c of $q^- = \lim_{r\to 0} q(r)$ and $q^+ = \lim_{r\to\infty} q(r)$ is 0.033333333.

[a] $r_0 = 30$.

TABLE III

Eigenvalues E^{PM} Computed by the Present Method (PM) with the Numerov Integrator[a] for Several Values of l and Compared to the Exact Values E^c of the Coulomb Potential

l	E^c	dE	r_0	r_s	R
5	−0.027777778	2.5 (−7)[b]	30	2.8	121
10	−0.0082644628	1.2 (−7)	110	25	310
15	−0.0039062500	5.5 (−8)	240	77	565
20	−0.0022675737	2.0 (−8)	420	162	886
25	−0.0014792899	1.1 (−8)	650	283	1,270

Note. The discrepancy $dE = E^{PM} - E^c$ is given in column 3. For each l, the starting point r_0 and the obtained limit points r_s (~ 0) and R ($\sim\infty$) are given in the last columns. (All values in a.u.)

[a] The step size is $h = 0.1$.

[b] 4.0 (−7) stands for 4.0×10^{-7}.

TABLE IV

Values of q^+ and q^- Computed with the Numerov Integrator for Several Values of the Step Size h for $l=5$ and $E=E^c$

h	$\bar{q}$	dq	r_s	R
0.5	0.0333358	1.4 (−7)[a]	2.4	129
0.4	0.0333344	−2.2 (−7)	2.2	127
0.3	0.0333338	−1.7 (−8)	2.4	126
0.2	0.03333345	1.6 (−8)	2.4	124
0.1	0.03333331	1.7 (−8)	2.8	121
KVS	0.033333333	0.0 (−8)	1.5	164
Theory	0.033333333	—	0	

Note. For each h, the mean value $\bar{q}=(q^+ + q^-)/2$ is given along with the discrepancy $dq=\bar{q}-q^c$; the exact theoretical value q^c for the Coulomb potential is given in the last line after that obtained with the KVS integrator. In the last columns the obtained limit points r_s (~ 0) and R ($\sim \infty$) are given.

[a] 1.4 (−7) stand for 1.4×10^{-7}.

precision), and the value r_s of r for which the function $q(r)$ reaches its limit q^-. We verify that R and r_s are functions of l and that r_s is different from zero for all $l>0$. We notice that the present method is free from any prior guess of R or r_s.

For this application, the integrator used is the "Kobeissi variable-step integrator" (KVS) [7]. The computer used is a home computer (NewBrain AD giving eight significant figures). The "origin" r_0 of integration is $r_0=l(l+1)$, which is the minimum of the function $V(r)$; we verified, however, that the computed eigenvalue E^{PM} is independent from this (convenient) choice of r_0.

In Table II we give some illustrations of the behaviour of the function $q(r)$. These examples show how q^-, r_s, q^+, R are obtained and allow the reader to deduce the simplicity of the method and of the program which is available from the authors upon request.

This approach to the present problem may also be used with other integrators [8], namely that of Numerov used in [1–2]. We give in Table III some examples of eigenvalues computed by the canonical functions method with the Numerov integrator. In Table IV we compare the two integrators by computing q^+ and q^- with the Numerov integrator (for several values of the step-size h) when E is the theoretical values $E^c=-1/(l+1)^2$. We compare these values to those obtained with the KVS integrator and to the theoretical value q^c. We deduce from this table the higher accuracy of the KVS integrator.

The case $l=0$ requires special attention only when the Numerov integrator is used. The rapid variation of $q(r)$ in the vicinity of $r\sim 0$ requires the reduction of the step-size h in this region in order to detect the limit q^- of $q(r)$. This is done automatically with the KVS integrator that we recommand for this type of problem.

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