9

Thomas-Fermi atom model

In the Thomas-Fermi atom model [81, 82] there exists the so-called Thomas-Fermi equation

$$u''(x) = \sqrt{\frac{u^3(x)}{x}}, \tag{9.1}$$

subject to the boundary conditions

$$u(0) = 1, u(+\infty) = 0 \tag{9.2}$$

in the common case. The Thomas-Fermi atom model views the electrons in an atom as a gas and derives atomic structure in terms of the electrostatic potential and the electron density in the ground state. Equation (9.1) describes the spherically symmetric charge distribution concerning a multi-electron atom.

From (9.1) and (9.2) it holds that $u''(0) \to +\infty$. So, there exists a singularity at $x = 0$. The analytic approximations of the Thomas-Fermi equation were given by the variational approach [83, 84], the δ-expansion method [85, 86, 87], Adomian's decomposition method [88, 89, 90, 91], and so on [92, 93, 94, 95, 96, 97]. However, all of these results are analytic-numerical because numerical techniques had to be employed to gain the value of $u'(0)$. Recently, Liao [51] applied the homotopy analysis method to give, for the first time, an explicit, purely analytic solution of the Thomas-Fermi equation by means of the base functions

$$\left\{ (1+x)^{-n} \;\middle|\; n \geq 1 \right\}. \tag{9.3}$$

Although Liao's [51] solution is valid in the whole region, its convergence rate is slow for large x. In this chapter, using a set of base functions better than the above ones, we apply the homotopy analysis method to give a more efficient analytic expansion of Thomas-Fermi equations.

9.1 Homotopy analysis solution

9.1.1 Asymptotic property

Equation (9.1) can be rewritten by

$$x\,[u''(x)]^2 - u^3(x) = 0. \tag{9.4}$$

Under the transformation

$$\tau = 1 + \lambda\, x, \tag{9.5}$$

where λ is a constant parameter to be determined later, Equation (9.4) becomes

$$\lambda^3\,(\tau - 1)\,\left(\frac{d^2u}{d\tau^2}\right)^2 - u^3(\tau) = 0, \tag{9.6}$$

subject to the boundary conditions

$$u(1) = 1, \qquad u(+\infty) = 0. \tag{9.7}$$

Note that Equation (9.6) contains neither linear terms nor small/large parameters. So, its nonlinearity is very strong. According to (9.7), as $\tau \to +\infty$, $u(\tau) \to 0$ either algebraically or exponentially. However, from Equations (9.6) and (9.7), it is hard to determine the asymptotic property of $u(x)$ at infinity. So, let us first assume that $u(\tau) \to 0$ algebraically and that $u(\tau)$ has the asymptotic expression

$$u(\tau) \sim \tau^{\kappa} \qquad \text{as} \qquad \tau \to +\infty,$$

where κ is an unknown constant. Substituting it into Equation (9.6) and then balancing the main terms, we have

$$\kappa = -3. \tag{9.8}$$

Therefore, $u(\tau)$ can be expressed by the set of base functions

$$\left\{\tau^{-m} \mid m \geq 3\right\} \tag{9.9}$$

in the form

$$u(\tau) = \sum_{m=3}^{+\infty} c_m\, \tau^{-m}, \tag{9.10}$$

where c_m is a coefficient. This provides us with the so-called *rule of solution expression.*

9.1.2 Zero-order deformation equation

Under the *rule of solution expression* denoted by (9.10) and using the boundary conditions (9.7), it is straightforward to choose

$$u_0(\tau) = \tau^{-3} \tag{9.11}$$

as the initial guess of $u(\tau)$. From (9.6) and using the *rule of solution expression* denoted by (9.10), we choose the auxiliary linear operator

$$\mathcal{L}[\Phi(\tau;q)] = \left(\frac{\tau}{4}\right)\,\frac{\partial^2\Phi(\tau;q)}{\partial\tau^2} + \frac{\partial\Phi(\tau;q)}{\partial\tau} \tag{9.12}$$

with the property

$$\mathcal{L}\left(\frac{C_1}{\tau^3}+C_2\right)=0, \tag{9.13}$$

where C_1 and C_2 are coefficients. From Equation (9.6), we define the nonlinear operator

$$\mathcal{N}[\Phi(\tau;q)]=\lambda^3\ (\tau-1)\left[\frac{\partial^2\Phi(\tau;q)}{\partial\tau^2}\right]^2-\Phi^3(\tau;q), \tag{9.14}$$

where $\Phi(\tau;q)$ is an unknown function of τ and q. Let $\hbar$ denote a nonzero auxiliary parameter and $H(\tau)$ a nonzero auxiliary function, respectively. Then, we construct the zero-order deformation equation

$$(1-q)\ \mathcal{L}\left[\Phi(\tau;q)-u_0(\tau)\right]=\hbar\ H(\tau)\ q\ \mathcal{N}[\Phi(\tau;q)], \tag{9.15}$$

subject to the boundary conditions

$$\Phi(1;q)=1, \Phi(+\infty;q)=0, \tag{9.16}$$

where $q\in[0,1]$ is an embedding parameter.

From (9.11), it is straightforward to show that when $q=0$ the solution of Equations (9.15) and (9.16) is

$$\Phi(\tau;0)=u_0(\tau). \tag{9.17}$$

Since $\hbar\neq 0$ and $H(\tau)\neq 0$, when $q=1$, Equations (9.15) and (9.16) are equivalent to Equations (9.6) and (9.7), respectively, provided

$$\Phi(\tau;1)=u(\tau). \tag{9.18}$$

Thus, as q increases from 0 to 1, $\Phi(\tau;q)$ varies from the initial guess $u_0(\tau)$ to the exact solution $u(\tau)$ of Equations (9.6) and (9.7).

By Taylor's theorem and using (9.17), we can expand $\Phi(\tau;q)$ in the series of q in the form

$$\Phi(\tau;q)=u_0(\tau)+\sum_{k=1}^{+\infty}u_k(\tau)\ q^k, \tag{9.19}$$

where

$$u_k(\tau)=\frac{1}{k!}\ \frac{\partial^k\Phi(\tau;q)}{\partial q^k}\bigg|_{q=0}. \tag{9.20}$$

$\Phi(\tau;q)$ is also dependent upon the auxiliary parameter $\hbar$ and the auxiliary function $H(x)$. Assuming that $\hbar$ and $H(x)$ are properly chosen so that the series (9.19) converges at $q=1$, we have, using (9.18),

$$u(\tau)=u_0(\tau)+\sum_{k=1}^{+\infty}u_k(\tau). \tag{9.21}$$

It provides us with a relationship between the initial guess $u_0(x)$ and the exact solution $u(x)$ by the terms $u_k(x)\ \ (k\geq 1)$.

9.1.3 High-order deformation equations

For brevity, define

$$\vec{u}_n = \{u_0(\tau), u_1(\tau), u_2(\tau), \cdots, u_n(\tau)\}.$$

Differentiating the zero-order deformation equations (9.15) and (9.16) k times with respect to q and then setting $q = 0$ and finally dividing them by $k!$, we have the so-called high-order deformation equation

$$\mathcal{L}\left[u_k(\tau) - \chi_k u_{k-1}(\tau)\right] = \hbar\, H(\tau)\, R_k(\vec{u}_{k-1}, \tau), \tag{9.22}$$

subject to the boundary conditions

$$u_k(1) = 0, u_k(+\infty) = 0, \tag{9.23}$$

where χ_k is defined by (2.42) and

$$\begin{aligned} & R_k(\vec{u}_{k-1}, \tau) \\ = & \sum_{j=0}^{k-1} \left[\lambda^3\, (\tau - 1)\, u_j''(\tau)\, u_{k-1-j}''(\tau) - u_{k-1-j}(\tau) \sum_{i=0}^{j} u_i(\tau)\, u_{j-i}(\tau) \right]. \end{aligned} \tag{9.24}$$

Note that $u_k(\tau)$ $(k \geq 1)$ is governed by the linear equation (9.22) and the linear boundary conditions (9.23). Thus, according to (9.21), the homotopy analysis method in essence transfers the original nonlinear problem, governed by Equations (9.6) and (9.7), to an infinite number of linear sub-problems, governed by Equations (9.22) and (9.23). Note that such a kind of transformation does not need any small or large parameters at all.

Let $u_k^*(\tau)$ denote a special solution of the equation

$$\mathcal{L}[u_k^*(\tau)] = \hbar\, H(\tau)\, R_k(\vec{u}_{k-1}, \tau).$$

Then, using (9.13), the general solution of Equation (9.22) is

$$u_k(\tau) = \chi_k\, u_{k-1}(\tau) + u_k^*(\tau) + C_1\, \tau^{-3} + C_2, \tag{9.25}$$

where the coefficients C_1 and C_2 are determined by the boundary conditions (9.23). In this way we can successively solve the high-order deformation equations (9.22) and (9.23), provided $H(\tau)$ is known. Under the *rule of solution expression* denoted by (9.10), $H(\tau)$ should be in the form

$$H(\tau) = \tau^{\sigma}, \tag{9.26}$$

where σ is an integer to be determined. It is found that when

$$\sigma > 4,$$

the solution contains the term

$$\tau \ln \tau$$

that disobeys the *rule of solution expression* denoted by (9.10). When

$$\sigma < 4,$$

the coefficient of the term τ^{-4} is always zero and cannot be improved even if the order of approximation tends to infinity. This disobeys the *rule of coefficient ergodicity*. Thus, to obey the *rule of solution expression* denoted by (9.10) and the *rule of coefficient ergodicity*, we had to choose $\sigma = 4$ which uniquely determines the auxiliary function

$$H(\tau) = \tau^4. \tag{9.27}$$

Thereafter, it is straightforward to solve the high-order deformation equations (9.22) and (9.23), successively.

9.1.4 Recursive expressions

Considering the importance of Thomas-Fermi atom model, it is worthwhile to give an explicit analytic expression of its solution. It is found that $u_k(\tau)$ can be expressed by

$$u_k(\tau) = \sum_{n=0}^{2k} \frac{\alpha_{k,n}}{\tau^{n+3}}, \tag{9.28}$$

where $\alpha_{k,n}$ is a coefficient. Substituting this expression into the high-order deformation equations (9.22) and (9.23), we gain the recurrence formulae

$$\begin{aligned}\alpha_{k,j} &= \chi_k \chi_{2k-j}\ \alpha_{k-1,j} \\ &+ \frac{4\hbar\left[\chi_{2k+1-j}\left(\lambda^3\beta_{k,j+1} - \gamma_{k,j+1}\right) - \chi_j\ \lambda^3\beta_{k,j}\right]}{j(j+3)},\end{aligned} \tag{9.29}$$

$$\begin{aligned}\beta_{k,i} = \sum_{j=0}^{k-1} \sum_{n=\max\{0,i+2j-2k\}}^{\min\{2j,i-2\}} &(n+3)(n+4)(i+1-n) \\ &\times (i+2-n)\ \alpha_{j,n}\ \alpha_{k-1-j,i-n-2},\end{aligned} \tag{9.30}$$

$$\gamma_{k,i} = \sum_{j=0}^{k-1} \sum_{n=\max\{0,i+2j-2k\}}^{\min\{2j,i-2\}} \delta_{j,n}\ \alpha_{k-1-j,i-n-2}, \tag{9.31}$$

and

$$\delta_{j,n} = \sum_{i=0}^{j} \sum_{r=\max\{0,n+2i-2j\}}^{\min\{2i,n\}} \alpha_{i,r}\ \alpha_{j-i,n-r}, \tag{9.32}$$

respectively. From (9.23), we have

$$\alpha_{k,0} = -\sum_{n=1}^{2k} \alpha_{k,n}. \tag{9.33}$$

From (9.11) we gain the first coefficient

$$\alpha_{0,0} = 1. \tag{9.34}$$

Thus, using the above recurrence formulae and from the first coefficient $\alpha_{0,0} = 1$, we can calculate successively all other coefficients $\alpha_{k,n}$. Therefore, we obtain an explicit analytic solution of the Thomas-Fermi atom model in the form:

$$u(x) = \sum_{k=0}^{+\infty} \sum_{n=0}^{2k} \frac{\alpha_{k,n}}{(1+\lambda\, x)^{n+3}}. \tag{9.35}$$

The corresponding mth-order approximation is expressed by

$$u(x) \approx \sum_{k=0}^{m} \sum_{n=0}^{2k} \frac{\alpha_{k,n}}{(1+\lambda\, x)^{n+3}}, \tag{9.36}$$

which gives

$$u'(0) \approx -\lambda \sum_{k=0}^{m} \sum_{n=0}^{2k} (n+3)\alpha_{k,n} \tag{9.37}$$

and

$$u''(0) \approx \lambda^2 \sum_{k=0}^{m} \sum_{n=0}^{2k} (n+3)(n+4)\alpha_{k,n}. \tag{9.38}$$

9.1.5 Convergence theorem

THEOREM 9.1
If the series

$$u_0(\tau) + \sum_{k=1}^{+\infty} u_k(\tau)$$

is convergent, where $u_k(\tau)$ is governed by Equations (9.22) and (9.23) under the definitions (9.12), (9.24), and (2.42), it must be an exact solution of the Thomas-Fermi equation.

Proof: If the series is convergent, it holds

$$\lim_{m \to +\infty} u_m(\tau) = 0$$

and we can express it by

$$s(\tau) = u_0(\tau) + \sum_{k=1}^{+\infty} u_k(\tau).$$

Then, using (9.12), (9.22), and (2.42), we have

$$\begin{aligned}
\hbar\, H(\tau) \sum_{k=1}^{+\infty} R_k(\vec{u}_{k-1}, \tau) &= \lim_{m\to+\infty} \sum_{k=1}^{m} \mathcal{L}[u_k(\tau) - \chi_k u_{k-1}(\tau)] \\
&= \mathcal{L}\left\{ \lim_{m\to+\infty} \sum_{k=1}^{m} [u_k(\tau) - \chi_k u_{k-1}(\tau)] \right\} \\
&= \mathcal{L}\left[\lim_{m\to+\infty} u_m(\tau) \right] \\
&= 0,
\end{aligned}$$

which gives, since $\hbar \neq 0$ and $H(\tau) = \tau^4$,

$$\sum_{k=1}^{+\infty} R_k(\vec{u}_{k-1}, \tau) = 0$$

for any $\tau \geq 1$. Substituting (9.24) into the above expression and simplifying it, we obtain

$$\begin{aligned}
&\sum_{k=1}^{+\infty} R_k(\vec{u}_{k-1}, \tau) \\
&= \sum_{k=1}^{+\infty} \sum_{j=0}^{k-1} \left[\lambda^3(\tau - 1)\, u_j''(\tau)\, u_{k-1-j}''(\tau) - u_{k-1-j}(\tau) \sum_{i=0}^{j} u_i(\tau)\, u_{j-i}(\tau) \right] \\
&= \lambda^3\, (\tau - 1) \left[\sum_{k=0}^{+\infty} u_k''(\tau) \right]^2 - \left[\sum_{k=0}^{+\infty} u_k(\tau) \right]^3 \\
&= \lambda^3\, (\tau - 1) \left[\frac{d^2 s(\tau)}{d\tau^2} \right]^2 - s^3(\tau) \\
&= 0.
\end{aligned}$$

From (9.23) and (9.11), it holds

$$s(1) = 1, s(+\infty) = 0.$$

So, $s(\tau)$ satisfies Equations (9.6) and (9.7), and therefore is an exact solution of the original Thomas-Fermi equations (9.1) and (9.2). This ends the proof.

9.2 Result analysis

According to Theorem 9.1, we should ensure that the solution series (9.35) converges. Note that this series contains the auxiliary parameter $\hbar$ and the parameter λ, which influence its convergence region and rate. We should therefore focus on the choice of $\hbar$ and λ.

The energy of a neutral atom in the Thomas-Fermi model is determined by

$$E = \frac{6}{7}\left(\frac{4\pi}{3}\right)^{2/3} Z^{7/3}\, u'(0),$$

where Z is the unclear charge. So, the initial slope $u'(0)$ has an important physical meaning. Instead of investigating the influence of $\hbar$ and λ on the convergence of $u(x)$ in the whole region $0 \le x < +\infty$, first we consider the series of $u'(0)$. Clearly, $u'(0)$ is dependent of both $\hbar$ and λ. For any a given $\hbar$, we can investigate the influence of λ on the convergence of the series $u'(0)$ by regarding it as a function of λ and plotting the corresponding curves of $u'(0)$ versus λ, as shown in Figure 9.1 for $\hbar = -1, \hbar = -3/4$, and $\hbar = -1/2$. According to Theorem 9.1, $u'(0)$ should converge to the same value, corresponding to a nearly horizontal line segment in Figure 9.1. From this figure, it is clear that $u'(0)$ is convergent when $0.2 < \lambda < 0.3$ and $-1 \le \hbar \le -1/2$. Then, it is natural to choose

$$\lambda = 1/4.$$

To investigate the influence of $\hbar$ on the convergence region and rate of series $u'(0)$ in the case of $\lambda = 1/4$, we plot the corresponding $\hbar$-curves (see page 26 and §3.5.1) of $u'(0)$, as shown in Figure 9.2. $u'(0)$ is convergent in the region $-2 < \hbar < 0$ when $\lambda = 1/4$. Furthermore, it is found that, as long as the series of $u'(0)$ converges, the corresponding series of $u(x)$ is convergent in the whole region $0 \le x < +\infty$. So, the series (9.35) is convergent in the whole region $0 \le x < +\infty$ when $\lambda = 1/4$ and $-2 < \hbar < 0$. For example, when $\hbar = -1$ and $\lambda = 1/4$, the 10th-order approximation of (9.36) agrees well with the 100th-order approximation, as shown in Figure 9.3, clearly indicating the convergence of the corresponding solution series. The convergent analytic results of $u(x)$ by means of $\hbar = -1$ and $\lambda = 1/4$ are listed in Table 9.1. According to Theorem 9.1, it must be the exact solution of the Thomas-Fermi equation. The explicit analytic expression (9.35) when $\hbar = -1$ and $\lambda = 1/4$ may be regarded as a definition of the solution of the Thomas-Fermi equation.

Kobayashi [98] gave the numerical result

$$u'(0) = -1.588071. \tag{9.39}$$

The approximations of the initial slope $u'(0)$ given by (9.36) when $\hbar = -1$ and $\lambda = 1/4$ are listed in Table 9.2. Clearly, the error decreases as the order of approximation increases. However, the convergence rate of $u'(0)$ is much slower than that of $u(x)$, possibly due to the singularity at $x = 0$. We employ the homotopy-Padé method (see page 38 and §3.5.2) to gain more accurate approximations of the initial slope $u'(0)$, as shown in Table 9.3. The approximations of $u''(0)$ when $\hbar = -1$ and $\lambda = 1/4$ are listed in Table 9.4. The homotopy-Padé approximations of $u''(0)$ are listed in Table 9.5. Obviously, $u''(0)$ given by (9.35) tends to infinity; this indicates that the homotopy analysis method may handle nonlinear problems with singularity and strong nonlinearity.

At the beginning of this chapter we assume that $u(x)$ tends to zero algebraically as $x \to +\infty$. Under this assumption we obtain the convergent results of the original Thomas-Fermi equation in the whole region $0 \le x < +\infty$. Thus, this assumption seems to be reasonable. So, we have many reasons to believe that the solution of the Thomas-Fermi equation behaves algebraically at infinity. Note that it is hard to get this kind of conclusion by numerical techniques. This example also illustrates that we may employ the homotopy analysis method to get an accurate approximation of a nonlinear problem by means of assuming a set of base functions even if we know a little about its properties, and such a kind of assumption damages the method a little in practice.

Having not realized the importance of the asymptotic property at infinity and expressing $u(x)$ in the form

$$u(x) = \sum_{n=1}^{+\infty} \frac{a_n}{(1+x)^n},$$

Liao [51] employed the homotopy analysis method to give an explicit analytic solution of the Thomas-Fermi equation, which converges slowly for large x. So, for nonlinear problems in an infinite domain, it seems better to investigate asymptotic properties of solutions at infinity. This can considerably increase the convergence rate of approximate series. Note that the solution of the Thomas-Fermi equation can be expressed, respectively, by the base functions (9.3) and (9.10), and the approximation series given by the latter converges faster than that by the former. This indicates that, although the solution of the Thomas-Fermi equation seems unique, it can be expressed by different base functions, and there might even exist the best one among them.

TABLE 9.1
The convergent analytic results of $u(x)$ given by (9.36) when $\hbar = -1$ and $\lambda = 1/4$.

x	$u(x)$	x	$u(x)$
0.25	0.755202	4.25	0.0996979
0.50	0.606987	4.50	0.0919482
0.75	0.502347	4.75	0.0850218
1.00	0.424008	5.00	0.0788078
1.25	0.363202	6.00	0.0594230
1.50	0.314778	7.00	0.0460978
1.75	0.275451	8.00	0.0365873
2.00	0.243009	9.00	0.0295909
2.25	0.215895	10.0	0.0243143
2.50	0.192984	15.0	0.0108054
2.75	0.173441	20.0	0.00578494
3.00	0.156633	25.0	0.00347375
3.25	0.142070	50.0	0.000632255
3.50	0.129370	75.0	0.000218210
3.75	0.118229	100	0.000100243
4.00	0.108404	1000	1.3513×10^{-7}

TABLE 9.2
The initial slope $u'(0)$ given by (9.37) when $\hbar = -1$ and $\lambda = 1/4$ compared with Kobayashi's numerical result.

Order of approximation	$u'(0)$	Error (%)
10	-1.28590	19.03
20	-1.40932	11.26
30	-1.46306	7.87
40	-1.49236	6.03
50	-1.51063	4.88
60	-1.52309	4.09
70	-1.53211	3.52
80	-1.53895	3.09
90	-1.54430	2.76
100	-1.54860	2.49
110	-1.55214	2.26
120	-1.55509	2.07

TABLE 9.3
The $[m, m]$ Homotopy-Padé approximation of the initial slope $u'(0)$ given by (9.37) when $\hbar = -1$ and $\lambda = 1/4$ compared with Kobayashi's numerical result.

$[m, m]$	$u'(0)$	Error (%)
$[5, 5]$	-1.50419	5.28
$[10, 10]$	-1.54600	2.65
$[15, 15]$	-1.56437	1.49
$[20, 20]$	-1.56474	1.47
$[25, 25]$	-1.57666	0.72
$[30, 30]$	-1.558032	0.49
$[35, 35]$	-1.58187	0.39
$[40, 40]$	-1.58301	0.32
$[45, 45]$	-1.58388	0.26
$[50, 50]$	-1.58469	0.21
$[55, 55]$	-1.58538	0.17
$[60, 60]$	-1.58605	0.13

TABLE 9.4
The analytic approximations of $u''(0)$ given by (9.38) when $\hbar = -1$ and $\lambda = 1/4$.

Order of approximation	$u''(0)$
10	3.79
20	6.41
30	8.96
40	11. 49
50	14.01
60	16.52
70	19.03
80	21.54
90	24.04
100	26.55
110	29.05
120	31.56

TABLE 9.5
The $[m, m]$ Homotopy-Padé approximations of $u''(0)$ given by (9.38) when $\hbar = -1$ and $\lambda = 1/4$.

$[m, m]$	$u''(0)$
$[5, 5]$	122.7
$[15, 15]$	6087.7
$[30, 30]$	168917
$[40, 40]$	643063
$[50, 50]$	2.15707×10^6
$[60, 60]$	8.78329×10^6

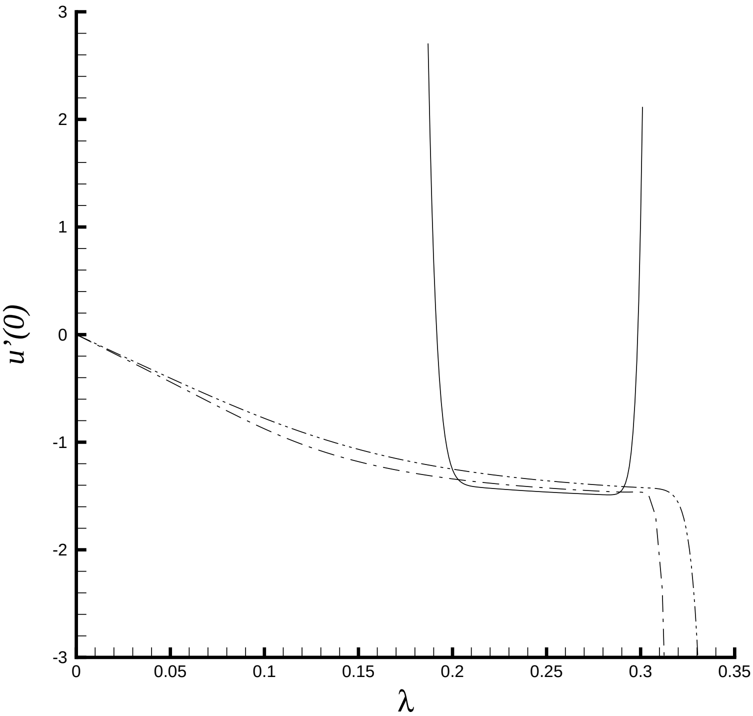

FIGURE 9.1
The 30th-order approximation of $u'(0)$ versus λ. Solid line: $\hbar = -1$; dash-dotted line: $\hbar = -3/4$; dash-dot-dotted line: $\hbar = -1/2$.

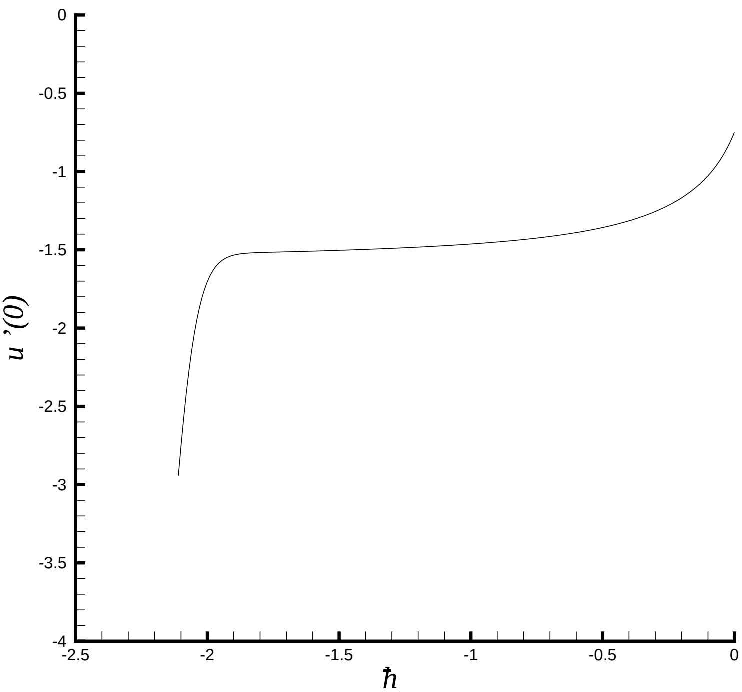

FIGURE 9.2
The $\hbar$-curve of $u'(0)$ at the 30th order of approximation when $\lambda = 1/4$.

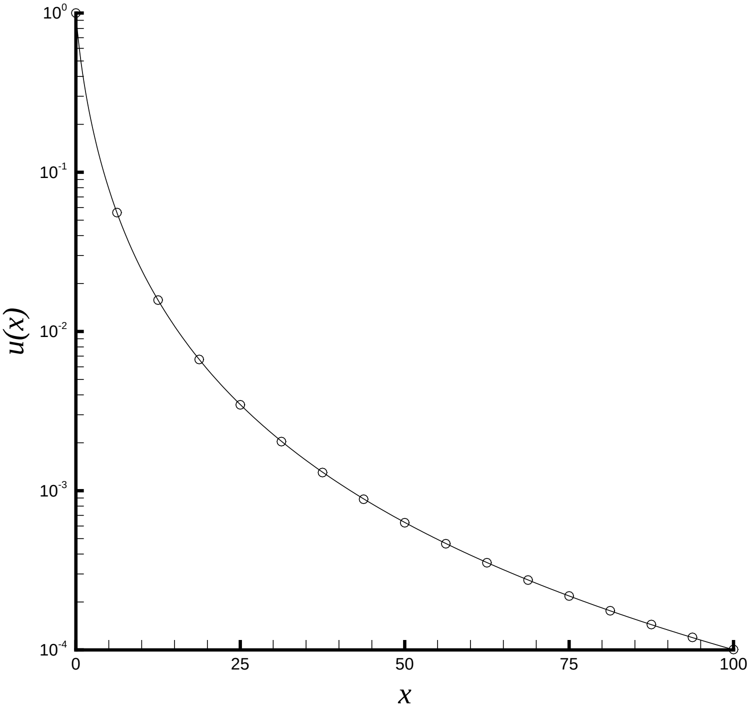

FIGURE 9.3
The analytic approximations of the Thomas-Fermi equation given by (9.36) when $\hbar = -1$ and $\lambda = 1/4$. Symbols: 10th-order approximation; solid line: 100th-order approximation.