

## CUBIC SPLINE METHOD FOR SOLVING SECOND-ORDER DIFFERENTIAL EQUATIONS: THEORY AND APPLICATION TO THE THOMAS–FERMI MODEL FOR IONS

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A cubic spline method is described which can be used to generate solutions to arbitrary second-order differential equations. The principle advantage is that this method provides accurate solutions which are cast in an analytic form, thus allowing the solutions to be applied to other problems. The method is applied to the solution of the Thomas–Fermi equation for singly and doubly ionized ions, and to the solution of the Schrödinger equation for the ground and first excited states of alkali metal atoms.

### 1. Introduction

Splines, which have become important tools in chemical physics for a variety of problems, are frequently used for fitting data, for interpolation and smoothing, and for generating potential energy curves and surfaces. However, a potential use of splines seems to have been overlooked: the application of splines to the direct solution of differential equations.

Previous work concerning the use of splines in the solution of differential equations [1,2] has focused on convergence properties and not on the applicability of splines to problems in chemical physics. In this report a method will be outlined for the use of cubic splines to solve arbitrary second-order differential equations. The principle advantage of this method is that the solutions are given in analytic form. Other advantages of this method are flexibility in the choice of the spline parameter as a function of the differential variable  $x$ , exact solutions at a chosen number of points along the interval of interest, and very simple and rapid execution.

The method is first outlined and then demonstrated by applications to the Thomas–Fermi equation for ions and to calculations of eigenvalues and eigenvectors for the ground and Rydberg states of alkali atoms. These two problems were chosen since the former involves nonstandard boundary conditions and both calculations provide situations where judicious

choices of the spline parameters yield quickly convergent solutions to the differential equations.

### 2. Cubic spline method for solving differential equations

The usual procedure for cubic spline fitting of data involves four steps:

(1) The interval of interest is divided into  $N$  sub-intervals,  $[x_i, x_{i+1}]$ ,  $i = 1, \dots, N$ . The spline knots,  $x_i$ , need not be evenly spaced.

(2) The form of the spline variable  $s$  is specified as a function of the variable  $x$ , and the spline function is specified by

$$f(s) = A_i \Delta s^3 + B_i \Delta s^2 + C_i \Delta s + f(s_i), \quad (1)$$

where

$$\Delta s = s - s_i.$$

This provides the spline representation of the data on the interval  $[x_i, x_{i+1}]$ .

(3) To insure that the functional form given by eq. (1) is smooth, we require the function and its first and second derivatives to be continuous at the knots,  $x_i$ . This provides three conditions:

$$A_i \Delta s_i^3 + B_i \Delta s_i^2 + C_i \Delta s_i + f(s_i) = f(s_{i+1}), \quad (2)$$

$$3A_i \Delta s_i^2 + 2B_i \Delta s_i + C_i = C_{i+1}, \quad (3)$$

$$3A_i \Delta s_i + B_i = B_{i+1}, \quad (4)$$

where

$$\Delta s_i = s_{i+1} - s_i.$$

(4) Finally, the values of  $f(x_i)$  for  $i = 1, \dots, N$  are supplied as well as two other pieces of data, usually either the first or second derivatives at the end points.

Here we consider an alternative situation. Suppose we have a differential equation which has been rearranged into the following form

$$G[x, f'(x), f''(x)] = f(x), \quad (5)$$

and suppose that  $f(x)$  has a known functional form at one of the boundaries (such that we can define the function and its first and second derivatives there), our problem is to evaluate  $f(x)$  given the form of  $G$  and the boundary conditions.

We can define the first and second derivatives of the cubic spline at the knot  $x_i$  as follows:

$$\left. \frac{\partial f}{\partial s} \right|_{s_i} = C_i, \quad (6)$$

$$\left. \frac{\partial^2 f}{\partial s^2} \right|_{s_i} = 2B_i. \quad (7)$$

Noting that

$$f'(x_i) = \frac{\partial s}{\partial x} \left. \frac{\partial f}{\partial s} \right|_{s_i} \quad (8)$$

and

$$f''(x_i) = \left[ \frac{\partial s}{\partial x} \right]^2 \left. \frac{\partial^2 f}{\partial s^2} \right|_{s_i} + \frac{\partial^2 s}{\partial x^2} \left. \frac{\partial f}{\partial s} \right|_{s_i}, \quad (9)$$

and using eqs. (2) through (4), we can write the derivatives at  $s_i$  in terms of those at  $s_{i+1}$ ,

$$\left. \frac{\partial f}{\partial s} \right|_{s_i} = \frac{1}{\Delta s_i} \left[ 3[f(s_{i+1}) - f(s_i)] - 2\Delta s_i \left. \frac{\partial f}{\partial s} \right|_{s_{i+1}} + \frac{1}{2} \Delta s_i^2 \left. \frac{\partial^2 f}{\partial s^2} \right|_{s_{i+1}} \right], \quad (10)$$

$$\left. \frac{\partial^2 f}{\partial s^2} \right|_{s_i} = \frac{1}{\Delta s_i^2} \left[ -6[f(s_{i+1}) - f(s_i)] + 6\Delta s_i \left. \frac{\partial f}{\partial s} \right|_{s_{i+1}} - 2\Delta s_i^2 \left. \frac{\partial^2 f}{\partial s^2} \right|_{s_{i+1}} \right]. \quad (11)$$

All of the elements of eq. (5) can thus be defined in terms of the function and its derivatives at  $x_{i+1}$  and  $f(x_i)$ .

Now, consider the situation when we know the functional behavior of our solution at the outer boundary point,  $x_{N+1}$ , and can define  $f(x_{N+1})$ ,  $f'(x_{N+1})$  and  $f''(x_{N+1})$ . Using eqs. (6)–(9) followed by (2)–(4), we can define  $f'(x_N)$  and  $f''(x_N)$  as linear equations in one unknown,  $f(x_N)$ . Substitution of these into eq. (5) provides us with a single nonlinear equation to solve for  $f(x_N)$  which we can do iteratively. Once  $f(x_N)$  is known, the process can be repeated for  $f(x_{N-1})$ , ... until we have reached our inner boundary point,  $x_1$ . The reverse procedure, that of starting at the inner boundary point,  $x_1$ , is done in the identical fashion except that now we define  $f(x_1)$ ,  $f'(x_1)$ , and  $f''(x_1)$  and proceed to solve for  $f(x_2)$ . In either case, application of eqs. (2) through (9) will subsequently yield values of  $A_i$ ,  $B_i$  and  $C_i$  for each interval, thus providing all the variables needed to express the solution to eq. (5) using eq. (1). Thus these equations provide all the information needed to solve the differential equation (5) with an analytic spline solution, such that eq. (5) is obeyed exactly at each knot and the first and second derivatives are all continuous at the knots. Clearly, the power of this method lies principally in the fact that the solution can be expressed in analytic form, as a series of spline functions given by eq. (1). Thus the solution can then be used directly to interpolate between knots or can be supplied in an analytic form for application to other problems. This will be demonstrated in the next section, with an application of the spline method to the Thomas–Fermi equations for ions.

To summarize, we follow the procedure for cubic spline fitting as given in steps (1) through (3) above and replace step (4) with (4'):

(4') Eq. (5) is to be obeyed at the knots and values for  $f(x_{N+1})$ ,  $f'(x_{N+1})$  and  $f''(x_{N+1})$  or values for  $f(x_1)$ ,  $f'(x_1)$  and  $f''(x_1)$  will be supplied. In many cases, one of these last function values will be necessary only as a normalization constant for the function.

Finally, explicit values of  $A_i$ ,  $B_i$  and  $C_i$  can be found from eqs. (2) through (7) once the values of  $f$ ,  $f'$  and  $f''$  are solved for at each knot.

### 3. Thomas–Fermi equation for ions

The Thomas–Fermi equation for ions is simply stated but not simply evaluated [3–5]. The differential equation is

$$\partial^2 \phi(x) / \partial x^2 = x^{-1/2} \phi^{3/2}(x), \quad (12)$$

and the difficulty for ionic systems arises from the non-standard boundary conditions,

$$\phi(0) = 1, \quad (13)$$

$$\phi(x_0) = 0. \quad (14)$$

The variable  $x$  is proportional to the radius  $r$  (in atomic units) as follows

$$x = rZ^{1/3}/0.885341, \quad (15)$$

and the Thomas–Fermi function  $\phi(r)$  is related to the potential function for the ion by

$$\phi(r) = r[V(r) - V_0]/Ze, \quad (16)$$

where  $V_0$  is the potential at  $r_0$ :

$$V_0 = (Z - N)e/r_0. \quad (17)$$

Here  $Z$  is the nuclear charge of the ion,  $N$  is the number of electrons and  $x_0$  (or  $r_0$  in atomic units) is the effective ionic radius, i.e. the radius outside of which the effective nuclear charge is  $(Z - N)e$ . In other words,

$$V(r) = (Ze/r)\phi(r) + V_0, \quad r \leq r_0, \quad (18)$$

$$V(r) = (Z - N)e/r, \quad r \geq r_0.$$

For neutral atoms,  $x_0$  is infinite and all atoms have the same Thomas–Fermi function  $\phi(x)$ . However, for ionic species, the right-hand boundary condition (14) is dependent on  $x_0$  which is in turn dependent on the ionic charge and number of electrons. Thus, each ion will be governed by a different Thomas–Fermi function.

Previous determinations of ionic properties using the Thomas–Fermi equation [3,4] involved numerical integration of eq. (1) while simultaneously optimizing the value of  $x_0$ . This can be a lengthy process since many steps may be necessary in the integration to yield accurate results. We find the Thomas–Fermi equation is well suited to a solution using cubic spline functions; indeed, the ionic form of the equations

proves to be an advantage to our method rather than a hindrance.

We first consider the form of  $s(x)$  that will allow the best cubic spline representation for the Thomas–Fermi ion problem. When the boundary conditions (13) and (14) are applied to eqs. (1) and (12), it is found that exact solutions to eq. (12) are possible if  $s = x, x^{1/2}$  or  $x^{1/3}$  as  $x \rightarrow 0$  and  $s = x^{1/2}, x^{3/2}$  or  $x^{3/4}$  as  $x \rightarrow x_0$ . Since  $s = x^{1/2}$  provides an exact result at both end-points, it will be chosen as our spline variable in eq. (1), where  $f(s) = \phi(s)$ .

We now need to consider whether any other information is necessary to completely determine the coefficients of the spline functions (1). Choosing  $s = x^{1/2}$ , requiring that the cubic spline functions and their first and second derivatives be continuous at the knots, and requiring that eq. (10) be satisfied at the knots gives us the following set of equations relating the spline parameters in the interval  $[x_i, x_{i+1}]$  to those in the interval  $[x_{i+1}, x_{i+2}]$ :

$$\begin{aligned} \phi_i^{3/2} = [3(s_i + s_{i+1})(\phi_i - \phi_{i+1}) + 2(2s_i + s_{i+1})C_{i+1}\Delta s_i \\ - (3s_i + s_{i+1})B_{i+1}\Delta s_i^2]/4s_i^2\Delta s_i^2, \end{aligned} \quad (19)$$

$$A_i = [\phi_{i+1} - \phi_i - C_{i+1}\Delta s_i + B_{i+1}\Delta s_i^2]/\Delta s_i^3, \quad (20)$$

$$B_i = [-3(\phi_{i+1} - \phi_i) + 3C_{i+1}\Delta s_i - 2B_{i+1}\Delta s_i^2]/\Delta s_i^2, \quad (21)$$

$$C_i = [3(\phi_{i+1} - \phi_i) - 2C_{i+1}\Delta s_i + B_{i+1}\Delta s_i^2]/\Delta s_i, \quad (22)$$

where

$$\Delta s_i = s_{i+1} - s_i, \quad \phi_i = \phi(s_i).$$

Given the values of  $\phi_{i+1}, B_{i+1}, C_{i+1}, s_i$  and  $s_{i+1}$ , these four equations completely determine the values of  $\phi_i, A_i, B_i$ , and  $C_i$ . Therefore, if we can fix  $\phi_{i+1}, B_{i+1}, C_{i+1}$  for  $x_{i+1} = x_0$ , we can determine all the spline parameters up to the origin. Since we know the form of the potential at  $x = x_0$  from eqs. (16), (17) and (18), we can obtain these values for a chosen value of  $x_0$  and completely determine the system of spline functions from eqs. (19)–(22). We can then converge asymptotically to the origin, compare the computed value of  $\phi(0)$  to eq. (13), correct our choice for  $x_0$  and recalculate the splines. This is repeated until  $\phi(0) = 1$  to within the accuracy desired.

In theory, as the number of knots goes to infinity ( $\Delta s_i \rightarrow 0$ ), the spline solution should converge to an

Table 1  
Effect of spline stepsize on Thomas–Fermi radii for Na<sup>+</sup>

| $\Delta s$ a) | $N$ b) | $x_0$   |
|---------------|--------|---------|
| 0.2           | 27     | 11.5744 |
| 0.1           | 43     | 11.5950 |
| 0.05          | 76     | 11.6020 |
| 0.025         | 144    | 11.6036 |
| 0.0125        | 279    | 11.6040 |

a) Initial step size:  $x_N^{1/2} - x_{N-1}^{1/2}$ .

b) Number of spline knots.

Table 2  
Radii of singly-ionized Thomas–Fermi ions a)

| Ion             | $Z$ | $N$ b) | Spline | Ref. [1] | Ref. [2] |
|-----------------|-----|--------|--------|----------|----------|
| He <sup>+</sup> | 2   | 75     | 2.952  |          |          |
| Li <sup>+</sup> | 3   | 94     | 4.590  | 4.589    | 4.586    |
| Na <sup>+</sup> | 11  | 144    | 11.604 | 11.609   | 11.60    |
| K <sup>+</sup>  | 19  | 165    | 15.677 | 15.685   | 15.67    |
| Cu <sup>+</sup> | 29  | 183    | 19.425 |          | 19.42    |
| Rb <sup>+</sup> | 37  | 194    | 21.856 | 21.874   | 21.84    |
| Ag <sup>+</sup> | 47  | 205    | 24.446 |          | 24.44    |
| Cs <sup>+</sup> | 55  | 212    | 26.291 | 26.319   | 26.29    |
| Au <sup>+</sup> | 79  | 229    | 30.925 |          | 30.92    |
| Fr <sup>+</sup> | 87  | 234    | 32.262 |          | 32.20    |

a) Radii given in Thomas–Fermi units: see eq. (15).

b) Number of spline knots –  $\Delta s = 0.025$ .

Table 3  
Radii of doubly ionized Thomas–Fermi ions a)

| Ion              | $Z$ | $N$ | Spline |
|------------------|-----|-----|--------|
| Bc <sup>2+</sup> | 4   | 76  | 2.952  |
| Mg <sup>2+</sup> | 12  | 120 | 7.930  |
| Ca <sup>2+</sup> | 20  | 139 | 10.972 |
| Sr <sup>2+</sup> | 38  | 165 | 15.677 |
| Ba <sup>2+</sup> | 56  | 182 | 19.092 |
| Ra <sup>2+</sup> | 88  | 202 | 23.719 |
| V <sup>2+</sup>  | 23  | 146 | 11.906 |
| Cr <sup>2+</sup> | 24  | 146 | 12.200 |
| Mn <sup>2+</sup> | 25  | 148 | 12.486 |
| Fe <sup>2+</sup> | 26  | 150 | 12.765 |
| Co <sup>2+</sup> | 27  | 151 | 13.037 |
| Ni <sup>2+</sup> | 28  | 154 | 13.303 |
| Cu <sup>2+</sup> | 29  | 154 | 13.562 |
| Zn <sup>2+</sup> | 30  | 156 | 13.816 |

a) See table 2 for notations and definitions.

exact form for  $\phi(x)$ . In practice, we are limited by the numerical accuracy with which we can calculate the spline solution, but table 1 demonstrates for Na<sup>+</sup> how the resultant value calculated for  $x_0$  converges to a limiting value as the number of spline knots increases.

Spline representations of the Thomas–Fermi potentials were computed for several singly and doubly charged ions. In each case, the calculation was very fast (one to five seconds on a VAX-11/780 computer). The calculated values of the ionic radii in the reduced units given by eq. (15) are reported in tables 2 and 3. Previous results are included where such data are available. The spline results agree very well with the other methods. However, the spline method has a great advantage over standard numerical methods because it gives an analytic form for the Thomas–Fermi potential function which can then be used for the calculation of atomic properties. This is illustrated in the next section.

#### 4. Eigenvalues for excited states of alkali metal atoms

Given the Thomas–Fermi potential function for an alkali ion, we can solve the Schrödinger equation for the ground and excited states of the atom,

$$\hat{H}\Psi(r) = -\frac{1}{2}\nabla^2\Psi(r) + [V(r) - \epsilon]\Psi(r) = 0, \quad (23)$$

where

$$V(r) = -V_{TF}(r) + l(l+1)/2r^2. \quad (24)$$

Here  $l$  is the angular momentum quantum number,  $\epsilon$  is the eigenvalue, and  $V_{TF}(r)$  is the spline representation of the Thomas–Fermi potential for the singly ionized alkali atom, given by eq. (18).

It is convenient to define a new wavefunction,

$$\Gamma(r) = r\Psi(r). \quad (25)$$

Substitution into eq. (23) yields a simplified form for the hamiltonian

$$\hat{H}'\Gamma(r) = -\frac{1}{2}\Gamma''(r) + [V(r) - \epsilon]\Gamma(r) = 0. \quad (26)$$

We employ the following cubic spline form for  $\Gamma(r)$  in the interval  $[r_i, r_{i+1}]$ ,

$$\Gamma(r) = r^l(A_i\Delta s^3 + B_i\Delta s^2 + C_i\Delta s + D_i) e^{-E(r)}, \quad (27)$$

where  $E(r)$  is defined as

$$E(r) \equiv Z_{\text{eff}}(r)r/(n-d) = V_{TF}(r)r^2/(n-d), \quad (28)$$

and

$$\Delta s = r - r_i.$$

Here  $n$  is the principle quantum number and  $d$  is the quantum defect for the level under consideration,

$$\epsilon = -1/2(n-d)^2. \quad (29)$$

Note that  $Z_{\text{eff}}$  in eq. (28) is an effective nuclear charge defined in terms of the Thomas-Fermi potential energy such that

$$V_{\text{TF}}(r) = Z_{\text{eff}}(r)/r. \quad (30)$$

The advantage of this form for our spline representation of the wavefunction is that it is exact for low lying states of the hydrogen atom.

In order to solve the hamiltonian (26) for  $\Gamma(r)$  and  $\epsilon$ , we proceed as follows:

(1) Choosing a value for the quantum defect,  $d$ , we begin at an outer radius  $r = r_\infty$ , where  $\Gamma(r)$  is small in magnitude. We then integrate eq. (26) backward from  $r_\infty$ , using the cubic spline method, until we reach the first maximum or minimum in  $\Gamma(r)$ , at a value of  $r$  denoted by  $r_0$ .

(2) Using the same value of  $d$ , we integrate eq. (26) forward from  $r = 0$  to  $r_0$  and evaluate the first derivative of  $\Gamma(r)$  there,  $\Gamma'_+(r_0)$ .

(3) If the chosen value for  $\epsilon$  is optimal,  $\Gamma'_+(r_0)$  will be zero. If the chosen value of  $\epsilon$  does not produce  $\Gamma'_+(r_0) = 0$ , then a new value of  $\epsilon$  is selected and the process iterated until the optimal  $\epsilon$  is found.

In order to use this procedure with a spline method of solution, we must be able to evaluate  $\Gamma(r)$ ,  $\Gamma'(r)$  and  $\Gamma''(r)$  at  $r = 0$  and  $r_\infty$ .

At the outer boundary,  $r_\infty$ , where  $V_{\text{TF}}(r)$  behaves as  $r^{-1}$ , we chose the following form for a hydrogen-like wavefunction,

$$\Gamma_{\text{H}}^{\infty}(r) = \exp\left[-\frac{r}{(n-d)}\right] \sum_{j=0}^{n-l-1} b_j r^{j+l-d+1}, \quad (31)$$

where the  $b_j$  are defined by

$$b_{j+1} = \frac{2}{(n-d)} \frac{[j+l+1-n]}{[j+1-d][j+2+2l-d]} b_j. \quad (32)$$

Substitution of eqs. (31) and (32) into eq. (26) gives the following error:

$$\begin{aligned} \hat{H}' \Gamma_{\text{H}}^{\infty}(r) = & -d(2l+1-d) b_0 r^{l-d-1} \\ & \times \exp[-r/(n-d)], \end{aligned} \quad (33)$$

which will be small at large  $r$ .

Thus we evaluate  $\Gamma(r_\infty)$ ,  $\Gamma'(r_\infty)$  and  $\Gamma''(r_\infty)$  from  $\Gamma_{\text{H}}^{\infty}(r_\infty)$ ,  $\Gamma_{\text{H}}^{\infty}'(r_\infty)$  and  $\Gamma_{\text{H}}^{\infty}''(r_\infty)$ . This gives us all of the information needed to proceed with the spline solution from  $r_\infty$  to  $r_0$ .

At the inner boundary,  $r = 0$ ,  $V_{\text{TF}}$  behaves as  $Z/r$ . If we substitute eq. (27) into eq. (26) and take the limit as  $r \rightarrow 0$ , we find

$$\Gamma(0) = D_1 = 0, \quad (34)$$

$$\Gamma'(0) = C_1, \quad (35)$$

and

$$\Gamma''(0) = B_1 = -ZC_1 [1 - (l+1)/(n-d)] / (l+1), \quad (36)$$

where  $C_1$  can be chosen as a normalization constant.

If we now proceed in the forward direction to solve for the spline solution to eq. (26), we obtain  $A_1$  from application of the solution at  $r_2$  and each  $A_i$  from the

Table 4  
Quantum defects for Na

| $(n, l)$ | $N^a$ | $d^b$ (calc) | $d^b$ (expt) |
|----------|-------|--------------|--------------|
| (3, 0)   | 27    | 1.454        | 1.373        |
|          | 43    | 1.432        |              |
|          | 76    | 1.427        |              |
|          | 144   | 1.426        |              |
|          | 279   | 1.425        |              |
| (4, 0)   | 27    | 1.529        | 1.357        |
|          | 43    | 1.439        |              |
|          | 76    | 1.415        |              |
|          | 144   | 1.409        |              |
|          | 279   | 1.408        |              |
| (3, 1)   | 27    | 1.074        | 0.883        |
|          | 43    | 0.956        |              |
|          | 76    | 0.925        |              |
|          | 144   | 0.917        |              |
|          | 279   | 0.915        |              |
| (3, 2)   | 27    | 0.019        | 0.010        |
|          | 43    | 0.014        |              |
|          | 76    | 0.014        |              |
|          | 144   | 0.013        |              |
|          | 279   | 0.013        |              |

a) Number of spline knots.

b) Calculated and experimental values for the quantum defect.

solution at  $r_{i+1}$ . We then proceed to evaluate the spline solution from  $r = 0$  to  $r = r_0$  and obtain  $\Gamma'_+(r_0)$ . The iteration for  $\epsilon$  is then carried out as described.

Tables 4 and 5 report results of such calculations for the eigenvalues of the ground and first few excited states of alkali metal atoms. The value of  $r_\infty$  was chosen to make the error term in eq. (31) less than  $10^{-6}$  atomic units. The spline knots were chosen according to the results of the spline fits to the Thomas–Fermi potentials. For  $0 \leq r \leq r_0$ , the knots from the Thomas–Fermi spline potential were used. For  $r_0 \leq r \leq r_\infty$ , the knots were chosen so that

$$\Delta r = r_N - r_{N-1}, \quad (37)$$

where  $r_N = r_0$  and  $r_{N-1}$  is the  $(N - 1)$ st spline knot from the Thomas–Fermi potential. Table 4 lists the

quantum defects calculated for Na using each of the Thomas–Fermi spline potentials reported in table 2. Convergence to a particular quantum defect is seen to proceed quickly and monotonically as the stepsize decreases in the Thomas–Fermi spline potential. Table 5 gives the quantum defects and energies of the ground states and first excited s, p and d states for the other alkali metal atoms. The Thomas–Fermi results are in remarkable agreement with the experimental values. The largest errors in each case arise for the ground state energies, but that is not surprising since we are modeling the atom as a frozen ionic core plus an electron in an outer orbital. Hence we expect that for the more Rydberg-like atomic states, the accuracy of this model would improve. For the excited state energies the errors increase as the nuclear charge

Table 5  
Quantum defects and eigenvalues for alkali atoms <sup>a)</sup>

| Atom | ( <i>n</i> , <i>l</i> ) | <i>d</i> (calc) <sup>b)</sup> | $\epsilon$ (calc) <sup>c)</sup> | <i>d</i> (expt) <sup>b)</sup> | $\epsilon$ (expt) <sup>c)</sup> |
|------|-------------------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|
| Li   | (2, 0)                  | 0.370                         | -0.1882                         | 0.411                         | -0.1981                         |
|      | (3, 0)                  | 0.367                         | -0.0721                         | 0.363                         | -0.0719                         |
|      | (2, 1)                  | 0.037                         | -0.1298                         | 0.041                         | -0.1302                         |
| Na   | (3, 0)                  | 1.426                         | -0.2018                         | 1.373                         | -0.1888                         |
|      | (4, 0)                  | 1.409                         | -0.0745                         | 1.357                         | -0.0716                         |
|      | (3, 1)                  | 0.917                         | -0.1152                         | 0.883                         | -0.1116                         |
|      | (3, 2)                  | 0.013                         | -0.0560                         | 0.010                         | -0.0559                         |
| K    | (4, 0)                  | 2.083                         | -0.1360                         | 2.230                         | -0.1592                         |
|      | (5, 0)                  | 2.069                         | -0.0582                         | 2.198                         | -0.0637                         |
|      | (6, 0)                  | 2.070                         | -0.0324                         | 2.190                         | -0.0344                         |
|      | (4, 1)                  | 1.620                         | -0.0882                         | 1.768                         | -0.1003                         |
|      | (3, 2)                  | 0.046                         | -0.0573                         | 0.146                         | -0.0614                         |
| Rb   | (5, 0)                  | 3.109                         | -0.1398                         | 3.195                         | -0.1535                         |
|      | (6, 0)                  | 3.090                         | -0.0591                         | 3.155                         | -0.0618                         |
|      | (5, 1)                  | 2.646                         | -0.0902                         | 2.707                         | -0.0951                         |
|      | (4, 2)                  | 1.123                         | -0.0604                         | 1.233                         | -0.0653                         |
| Cs   | (6, 0)                  | 3.855                         | -0.1087                         | 4.131                         | -0.1431                         |
|      | (7, 0)                  | 3.836                         | -0.0499                         | 4.080                         | -0.0586                         |
|      | (6, 1)                  | 3.412                         | -0.0746                         | 3.638                         | -0.0896                         |
|      | (5, 2)                  | 2.074                         | -0.0584                         | 2.452                         | -0.0770                         |
| Fr   | (7, 0)                  | 3.834                         | -0.0499                         |                               |                                 |
|      | (8, 0)                  | 3.834                         | -0.0288                         |                               |                                 |
|      | (7, 1)                  | 4.424                         | -0.0754                         |                               |                                 |
|      | (6, 2)                  | 3.114                         | -0.0600                         |                               |                                 |

<sup>a)</sup> Spline results for TF potentials are given in table 2.

<sup>b)</sup> Quantum defects.

<sup>c)</sup> Energies in hartrees relative to ion. Experimental values are from ref. [6].

increases, probably due to the lack of polarization terms and exchange terms in the Thomas–Fermi approximation. Nonetheless, the worst errors are on the order of 0.02 hartree and the correct trends in energies and quantum defect are obtained. Thus the Thomas–Fermi approximation, coupled with the assumption of a frozen ionic core, seems to do quite well in predicting energies of alkali metal atoms.

## 5. Conclusions

Second-order differential equations can be readily solved using cubic splines. The principal advantage of this method is that it produces an analytic form for the solution which can then be used for other problems. Thus, the Thomas–Fermi potential evaluated here might be employed as an effective potential in model calculations for molecules containing alkali metal atoms. Splines are easy to work with, the method requires little computer time, and convergence to a limiting eigenvalue occurs quickly and smoothly with increase in the number of spline knots. As illustrated here, the resultant spline form of the Thomas–Fermi potential has a convenient form for solving the Schrödinger equation, again using splines.

We are now considering the application of this method to the solutions of the Schrödinger equation

for  $\text{H}_2^+$ ,  $\text{HeH}^{2+}$ , to the  $n$ -dimensional form of the Thomas–Fermi problem and to the Hartree–Fock method for atoms.

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