Simulator of photoemission angular dictribution for experiments (SPADExp)
2. Calculations of atomic potentials

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Abstract

We explain the process to numerically calculate atomic potentials based on Hartree-Fock-Slater (HFS) equations.

Contents

1 Numerical solutions of differential equations

1.1 Reduction to first-order differential equations

The differential equations in the following discussions can be represented by the form of

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2} f(x) = F(f(x),\ x) \tag{1}$$

and are solved in $x \geq 0$ region. Some of them satisfy the relationship $F(f(x),\ x) = -a(x) \cdot f(x)$[1]. Using $f'(x) = \frac{\mathrm{d}}{\mathrm{d}x} f(x)$, we can transform the equations to a first-order differential equation like

$$\frac{\mathrm{d}}{\mathrm{d}x} \begin{pmatrix} f(x) \\ f'(x) \end{pmatrix} = \begin{pmatrix} f'(x) \\ F(f(x),\ x) \end{pmatrix}. \tag{2}$$

[1] The minus sign is to match the Numerow method.

1.2 Euler method

Euler method calculates the value at x_{i+1} using only the value at x_i. We take a sequence of points x_i $(i = 0,\ 1,\ \cdots)$ in $x \geq 0$ region satisfying $0 = x_0 < x_1 < \cdots < x_i < x_{i+1} < \cdots$; the distances between two adjacent points $x_{i+1} - x_i$ need not to be uniform. Also, we suppose that the initial values $f(0),\ f'(0)$ are given. In this situation, the values at x_{i+1}, $f(x_{i+1})$ and $f'(x_{i+1})$ can be calculated from those at x_i by the following equations;

$$f(x_{i+1}) = f(x_i) + f'(x_i)(x_{i+1} - x_i) \tag{3}$$
$$f'(x_i) = f'(x_i) + F(f(x_i), x_i)(x_{i+1} - x_i). \tag{4}$$

Although Euler method is less precise than following methods because the error is proportional to the step width [3], it is more general because it does not require an equally-separated grid.

1.3 4th-order Runge-Kutta method

First we describe the general form of 4th-order Runge-Kutta method. We suppose a first-order differential equation of a vertical vector $\mathbf{y}(x)$ like

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathbf{y}(x) = f(\mathbf{y}(x),\ x), \tag{5}$$

where $f(\mathbf{y}(x),\ x)$ is a function which returns a vertical vector of the same dimension as $\mathbf{y}(x)$. Using sequence of points x_i equally-separated with the distance h, $\mathbf{y}_{i+1}$ can be calculated by

$$\mathbf{k}_1 = f(\mathbf{y}(x_i),\ x_i) \tag{6}$$
$$\mathbf{k}_2 = f(\mathbf{y}(x_i) + h\mathbf{k}_1/2,\ x_i + h/2) \tag{7}$$
$$\mathbf{k}_3 = f(\mathbf{y}(x_i) + h\mathbf{k}_2/2,\ x_i + h/2) \tag{8}$$
$$\mathbf{k}_4 = f(\mathbf{y}(x_i) + h\mathbf{k}_3,\ x_i + h) \tag{9}$$
$$\mathbf{y}_{i+1} = \mathbf{y}_i + h\left[\frac{1}{6}\mathbf{k}_1 + \frac{1}{3}\mathbf{k}_2 + \frac{1}{3}\mathbf{k}_3 + \frac{1}{6}\mathbf{k}_4\right]. \tag{10}$$

This method gives the error proportional to the 4th power of the step h [3].

In our situation, 4th-order Runge-Kutta method becomes

$$k_1 = f'(x_i) \qquad k'_1 = F(f(x_i),\ x_i) \tag{11}$$
$$k_2 = f'(x_i) + hk'_1/2 \qquad k'_2 = F(f(x_i) + hk_1/2,\ x_i + h/2) \tag{12}$$
$$k_3 = f'(x_i) + hk'_2/2 \qquad k'_3 = F(f(x_i) + hk_2/2,\ x_i + h/2) \tag{13}$$
$$k_4 = f'(x_i) + hk'_3 \qquad k'_4 = F(f(x_i) + hk_3,\ x_i + h) \tag{14}$$
$$f(x_{i+1}) = f(x_i) + h\left[\frac{1}{6}k_1 + \frac{1}{3}k_2 + \frac{1}{3}k_3 + \frac{1}{6}k_4\right] \quad f'(x_{i+1}) = f'(x_i) + h\left[\frac{1}{6}k'_1 + \frac{1}{3}k'_2 + \frac{1}{3}k'_3 + \frac{1}{6}k'_4\right]. \tag{15}$$

1.4 Numerov method

Numerov can be used if the differential equation satisfies $F(f(x),\ x) = -a(x) \cdot f(x)$. We do not use a simultaneous differential equation form like above, but we calculate the value by the following equation;

$$f(x_{i+1}) = \frac{2(1 - 5h^2a(x_i)/12)f(x_i) - (1 + h^2a(x_{i-1})/12)f(x_{i-1})}{1 + h^2a(x_{i+1})/12}, \tag{16}$$

where h is the distance between two adjacent points and must be constant.

The above equation is derived as follows[3]. First, using Störmer's formula

$$f(x_{i+1}) - 2f(x_i) + f(x_{i-1}) = \frac{h^2}{12}\Big(F(f(x_{i+1}),\ x_{i+1}) + 10F(f(x_i),\ x_i) + F(f(x_{i-1}),\ x_{i-1})\Big) + O(h^6), \tag{17}$$

$F(f(x),\ x)$ terms in the RHS are replaced by $-a(x) \cdot f(x)$. Then gathering $f(x_{i+1})$ in the RHS, we get eq. (16).

Table 1: Default sequence of points.

First point index	Last point index	Distance	Number of distances	First point position	Last point position
0	40	0.0025	40	0	0.1
40	80	0.005	40	0.1	0.3
80	120	0.01	40	0.3	0.7
120	160	0.02	40	0.7	1.5
160	200	0.04	40	1.5	3.1
200	240	0.08	40	3.1	6.3
240	280	0.16	40	6.3	12.7
280	320	0.32	40	12.7	25.5
320	360	0.64	40	25.5	51.1
360	400	1.28	40	51.1	102.3
400	440	2.56	40	102.3	204.7

1.5 Sequence of points in actual calculations

In our program, sequence of points are separated by some blocks, and in each block points are equally separated. Table 1 describes the default sequence.

2 Calculations of the Thomas-Fermi potential

The differential equation for the Thomas-Fermi potential is

$$\frac{\mathrm{d}}{\mathrm{d}x^2}g(x) = F(g(x),\ x) = \frac{g(x)^{3/2}}{\sqrt{x}}. \tag{18}$$

Since Numerov method is not applicable to the equation, we solve it by Euler method or 4th-order Runge-Kutta method. We note that only Euler method is applicable when we consider points belonging to different blocks, because the distance is not uniform.

The boundary condition derives the initial value $g(0) = 1$, but $g'(0)$ can not be determined. Therefore, we need to find appropriate $g'(0)$ satisfying the other boundary condition $g(x) \to 0$ $(x \to \infty)$. In addition, if $g(x_i)$ becomes negative, we can not calculate $g(x_{i+1})$ and further because we cannot perform the three-halves power calculation.

In our actual calculations, we use the bisection method to find $g'(0)$ which gives $g(x_N)$ smaller than the threshold. Here we represent the value $g(x_N)$ calculated with the initial value $g'(0) = g'$ by $g(x_N;\ g')$; if $g(x_i) < 0$ occurs during calculations, we suppose $g(x_N;\ g') = g(x_i)$. The following is the detailed procedure of calculations.

1. Find g'_0 and g'_1, which satisfy $g(x_N;\ g'_0) < 0 < g(x_N;\ g'_1)$.
2. Take $g'_2 = (g'_0 + g'_1)/2$ and calculate $g(x_N;\ g'_2)$.
3. If $g(x_N;\ g'_2) < 0$, replace g'_0 by g'_2. If $g(x_N;\ g'_2) > 0$ and larger than the threshold, replace g'_1 by g'_2. If $g(x_N;\ g'_2) > 0$ and smaller than the threshold, current $g(x_i)$ is the solution.
4. Unless $g(x_N;\ g'_2) > 0$ and smaller than the threshold, go back to 2. and continue calculations.

Figure 1 represents $g(x)$ obtained by our numerical calculations, which is approximately equal to the previous research [2].

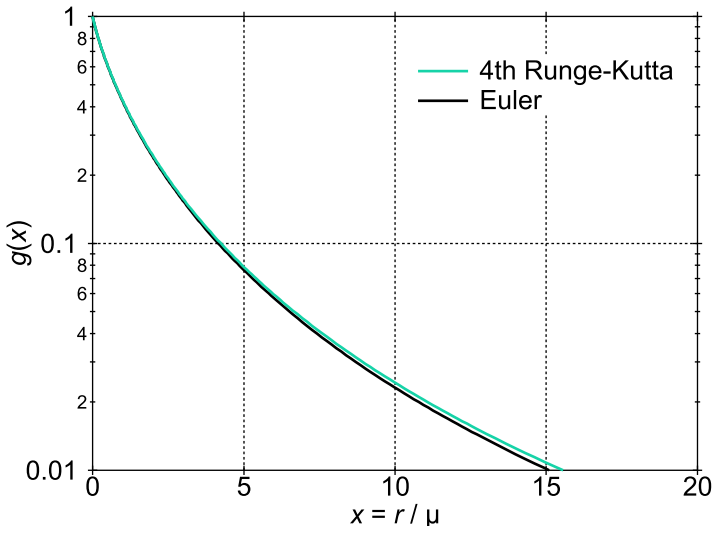

Figure 1: Thomas-Fermi potential function $g(x)$。

3 Schrödiger equation in an isotropic potential

3.1 Calculation procedure

The potential in the HFS equation $V(r)$ is isotropic, so we need to solve the Schrödinger equation of the radial part;

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{l(l+1)}{2r^2}+V(r)\right]P_{nl}(r)=E_{nl}P_{nl}(r). \tag{19}$$

Using the Thomas-Fermi scaling $r=\mu x$ and the substitution $P_{nl}(r)=p_{nl}(x),\ V(r)=v(x)$, we get

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}p_{nl}(x)=\left[\frac{l(l+1)}{x^2}+2\mu^2(v(x)-E_{nl})\right]p_{nl}(x). \tag{20}$$

Since the potential values at points x_i, $v(x_i)$, are given, we can use Euler method or Numerov method. We cannot use 4th-order Runge-Kutta method because it uses the value at $x_i+h/2$. We find the solution with $n-l-1$ nodes and eigenvalue E_{nl}. Bound solutions, which are regular at the origin, should satisfy $p_{nl}(0)=0$ and $p_{nl}(x)\to 0$ $(x\to\infty)$. The following condition is approximated to $p_{nl}(x_N)=0$, where x_N is the last point of calculations.

We can use similar procedure to that of the Thomas-Fermi potential, to obtain $p_{nl}(x_i)$ with initial conditions at the origin $p_{nl}(0)=0$; for $p'_{nl}(0)$ we can set an arbitrary value. However, this procedure gives large numerical error in large x region, so it is difficult to obtain E_{nl} satisfying $p_{nl}(x_N)=0$ by the bisection method. Therefore, we use the following procedure to calculate $p_{nl}(x_i)$ with given E_{nl}.

1. The function in the RHS of eq. (20), $l(l+1)/x^2+2\mu^2(v(x)-E_{nl})$, becomes $-E_{nl}>0$ in the limit $x\to\infty$. Therefore, if E_{nl} is an appropriate eigenvalue, $p_{nl}(x)$ increases/decreases monotonically and does not have a node in $x>x_0$ region, where x_0 is the last border across which the function changes sign (from negative to positive).

2. We set the calculation region to $0\le x<x_0\times$ const. An appropriate const. is around 8, and if the last point is smaller than $x_0\times$ const. the former is the calculation border.

3. We solve the differential equation from $x=0$ to outward in $0\le x\le x_0$ region and obtain$p^{\mathrm{out}}_{nl}(x_i)$. On the other hand, in $x_0\le x$ region the equation is solved from the border to inward and we obtain $p^{\mathrm{in}}_{nl}(x_i)$. In both calculations, the initial values of the differential are given arbitrarily.

4. We count the number of nodes only in $0\le x\le x_0$ region.

5. Since eq. (20) is a linear differential equation, a solution multiplied by a constant is also a solution. We can scale $p^{\mathrm{out}}_{nl}(x_i)$ and $p^{\mathrm{in}}_{nl}(x_i)$ so that they are continuous at $x=x_0$. If the differentials are also

continuous, the solution is appropriate. We can use the logarithmic derivative $\frac{1}{p_{nl}(x)}\frac{\mathrm{d}}{\mathrm{d}x}p_{nl}(x) = \frac{\mathrm{d}}{\mathrm{d}x}\log\big(p_{nl}(x)\big)$ to judge the continuity of the differential.

6. If the logarithmic derivatives do not coincide, We can estimate the error ΔE by the method in the following subsection.

First we perform 1.-4. to obtain largest E_{nl} with $n-l-1$ nodes[2]. After this estimation, we perform 1.-6. to change the estimated value of the eigenenergy. We continue this process until $|\Delta E|$ is smaller than the threshold, and then we obtain the eigenvalue E_{nl}, and the wavefunction is obtained by normalizing $p_{nl}(x_i)$.

3.2 Estimation of the eigenenergy error from logarithmis derivatives

Modifying eq. (20), we use the following differential equation

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}p(x) + (V(x)-\varepsilon)p(x) = 0 \tag{21}$$

and boundary conditions $p(0)=0,\ p(x)\to 0\ (x\to\infty)$, where $p(x)$ is the solution and ε is the eigenenergy. Using a solution $q(x) = p(x) + \Delta p(x)$ and eigenenergy $\varepsilon + \Delta\varepsilon$, which satisfies the boundary conditions but is not continuous or differentiable at $x = x_0$, we estimate the eigenenergy error $\Delta\varepsilon$.

Since $q(x)$ and $\varepsilon + \Delta\varepsilon$ satisfy eq. (21) at any point other than $x = x_0$, inserting them and taking the first order of the error, we obtain

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Delta p(x) + (V(x)-\varepsilon)\Delta p(x) - \Delta\varepsilon\cdot p(x) = 0. \tag{22}$$

Multiplying $p(x)$ and performing integration, we get

$$\int_0^{x_0}\Big[p(x)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Delta p(x) + (V(x)-\varepsilon)p(x)\Delta p(x) - \Delta\varepsilon\cdot p(x)^2\Big]\mathrm{d}x = 0 \tag{23}$$

$$\iff \int_0^{x_0}\Big[p(x)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Delta p(x) - \Delta p(x)\frac{\mathrm{d}^2}{\mathrm{d}x^2}p(x)\Big]\mathrm{d}x = \Delta\varepsilon\int_0^{x_0}p(x)^2\mathrm{d}x \quad (\because \text{Using eq. (21) to } (V(x)-\varepsilon)p(x)) \tag{24}$$

$$\iff \left[p(x)\frac{\mathrm{d}}{\mathrm{d}x}\Delta p(x) - \Delta p(x)\frac{\mathrm{d}}{\mathrm{d}x}p(x)\right]_0^{x_0} = \Delta\varepsilon\int_0^{x_0}p(x)^2\mathrm{d}x \tag{25}$$

$$\iff \left[p(x)^2\Delta\left(\frac{1}{p(x)}\frac{\mathrm{d}}{\mathrm{d}x}p(x)\right)\right]_0^{x_0} = \Delta\varepsilon\int_0^{x_0}p(x)^2\mathrm{d}x \tag{26}$$

$$\iff p(x_0)^2\Delta\left(\frac{1}{p(x_0)}\frac{\mathrm{d}}{\mathrm{d}x}p(x_0)\right) = \Delta\varepsilon\int_0^{x_0}p(x)^2\mathrm{d}x \quad (\because p(0)=0). \tag{27}$$

We can obtain the similar result by changing the integration region to $[x_0,\ \infty]$. Modifying these results by using $q(x)$, we get

$$p(x_0)^2\left[\frac{1}{q(x_0-0)}\frac{\mathrm{d}}{\mathrm{d}x}q(x_0-0) - \frac{1}{p(x_0)}\frac{\mathrm{d}}{\mathrm{d}x}p(x_0)\right] = \Delta\varepsilon\int_0^{x_0}p(x)^2\mathrm{d}x \tag{28}$$

$$-p(x_0)^2\left[\frac{1}{q(x_0+0)}\frac{\mathrm{d}}{\mathrm{d}x}q(x_0+0) - \frac{1}{p(x_0)}\frac{\mathrm{d}}{\mathrm{d}x}p(x_0)\right] = \Delta\varepsilon\int_{x_0}^{\infty}p(x)^2\mathrm{d}x. \tag{29}$$

We replace $p(x)$ by $q(x)$ because we cannot obtain $p(x)$, and modifying the equations to remove the second term in the LHS, we get

$$\Delta\varepsilon = \frac{\dfrac{1}{q(x_0-0)}\dfrac{\mathrm{d}}{\mathrm{d}x}q(x_0-0) - \dfrac{1}{q(x_0+0)}\dfrac{\mathrm{d}}{\mathrm{d}x}q(x_0+0)}{\dfrac{1}{q(x_0-0)^2}\displaystyle\int_0^{x_0}q(x)^2\mathrm{d}x + \frac{1}{q(x_0+0)^2}\int_{x_0}^{\infty}q(x)^2\mathrm{d}x}. \tag{30}$$

As you can see from the equation, we can use $p_{nl}^{\mathrm{out}}(x_i)$ and $p_{nl}^{\mathrm{in}}(x_i)$ without the scaling to the error estimation.

[2] If the energy increases slightly from E_{nl}, where E_{nl} is a solution satisfying the boundary and node-number conditions, the node increases by 1.

3.3 Calculation examples using Thomas-Fermi

Figure 2 shows the Z dependence of eigenenergies of the Schrödinger equation with the Thomas-Fermi potential. This result coincides well with the previous research [2].

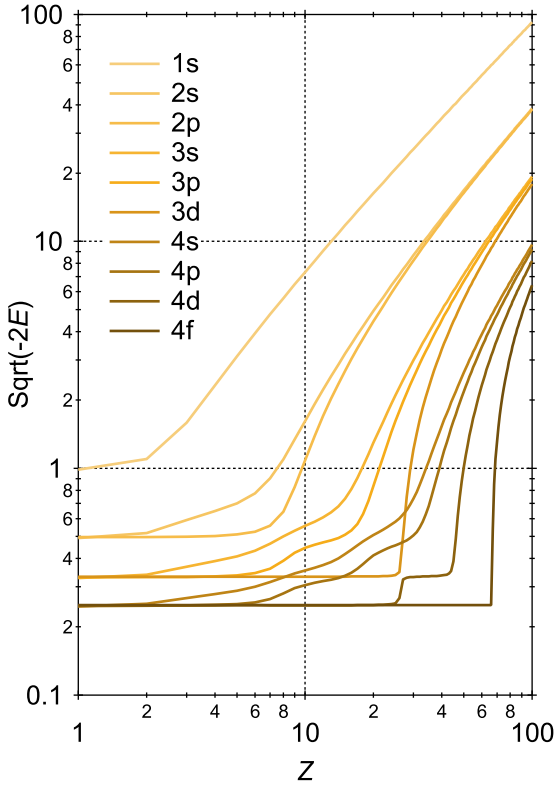

Figure 2: Eigenenergies in the Thomas-Fermi potential. Since the previous research [2] uses the Rydberg unit system, the vertical axis is $\sqrt{-2E}$, not $\sqrt{-E}$.

4 Calculations of self-consistent atomic potentials

4.1 Modification of the potential

As discussed above, the potential $V(r)$ in the HFS equation is given by

$$V(r) = -\frac{Z}{r} + \frac{1}{r}\int_0^r \sigma(r')\mathrm{d}r' + \int_r^\infty \frac{\sigma(r')}{r'}\mathrm{d}r' - 3\left(\frac{3\rho(r)}{8\pi}\right)^{1/3} \tag{31}$$

$$\sigma(r) = \sum_{nl} w_{nl}(P_{nl}(r))^2 \tag{32}$$

$$\rho(r) = \frac{\sigma(r)}{4\pi r^2}. \tag{33}$$

In our actual calculations, we use the scaling $r = \mu x$, so the equations become

$$V(x_i) = -\frac{Z}{\mu x_i} + \frac{1}{x_i}\sum_{j=0}^{i-1}\sigma(x_j)(x_{j+1} - x_j) + \sum_{j=i}^{N-1}\frac{\sigma(x_j)}{x_j}(x_{j+1} - x_j) - 3\left(\frac{3\rho(x_i)}{8\pi}\right)^{1/3} \tag{34}$$

$$\sigma(x_i) = \sum_{nl} w_{nl}(P_{nl}(x_i))^2 \tag{35}$$

$$\rho(x_i) = \frac{\sigma(x_i)}{4\pi(\mu x_i)^2}. \tag{36}$$

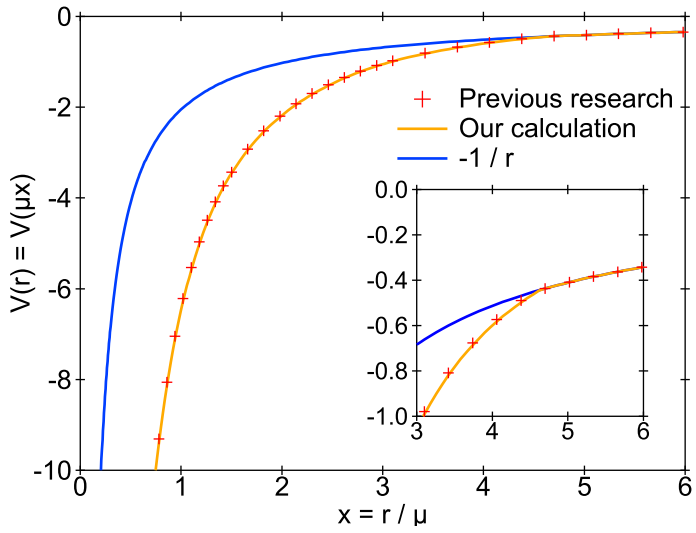

Figure 3: Self-consistent atomic potential of a carbon atom. The inset shows the border where the modification $V(x) = -1/\mu x$ starts.

Furthermore, the potential should satisfy $V(x_i) \sim -1/\mu x_i$ in $x \to \infty$ limit, so we add the following modification:

$$V_{\text{modified}}(x_i) = \begin{cases} V(x_i) & V(x_i) < -\dfrac{1}{\mu x_i} \\ -\dfrac{1}{\mu x_i} & V(x_i) > -\dfrac{1}{\mu x_i} \end{cases} . \tag{37}$$

The radial Schrödinger equation (20) with the modified potential $V_{\text{modified}}(x_i)$ is solved.

4.2 SCF convergence

the j-th calculation is performed using the j-th input potential $V^{(j)}(x_i)$, $V^{(j)}_{\text{modified}}(x_i)$. After that, the potential for the $j+1$-th calculation is obtained by the simple mixing method. We represent the potential obtained by the j-th calculation by $V(x_i)$, $V_{\text{modified}}(x_i)$, and then the $j+1$-th input is

$$V^{(j+1)}(x_i) = (1-A)V(x_i) + A \cdot V^{(j)}(x_i), \quad V^{(j+1)}_{\text{modified}}(x_i) = (1-A)V_{\text{modified}}(x_i) + A \cdot V^{(j)}_{\text{modified}}(x_i) \tag{38}$$

. The mixing ratio A is between 0 and 1, and $A = 0.5$ gave the appropriate convergence.

The convergence is checked by the following parameters α, β.

$$\alpha_j = \max_i \left| \frac{V^{(j)}(x_i) - V^{(j+1)}(x_i)}{V^{(j)}(x_i)} \right| \tag{39}$$

$$\beta_j = \max_i \left| \mu x_i V^{(j)}(x_i) - \mu x_i V^{(j+1)}(x_i) \right| \tag{40}$$

We finished the calculations when the both values are below the thresholds.

4.3 Calculation example

In case of the carbon atom, $Z = 6$ and the occupancy is $w_{10} = 2$, $w_{20} = 2$, $w_{21} = 2$. Figure 3 shows the calculation result in good coincidence with the previous research [1].

References

[1] F. Herman and S. Skillman "Atomic Structure Calculations " , 1963.

[2] R. Latter, Phys. Rev. **99**, 510 (1955).

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