Contents

List of Figures

Chapter 1

Scalar relativistic approximation and the spin orbit coupling

1.1 Dirac equation

Non-relativistic quantum mechanics has broad application, but when the speed of electron is near the speed of light, the non-relativistic quantum is not suitable to describe the system of electron. So Dirac introduced an equation which is called Dirac equation applying for relativistic case.
Dirac defined the Hamiltonian:

$$\hat{H}_{dirac} = c\boldsymbol{\alpha}\mathbf{P} + \boldsymbol{\beta}mc^2 + V \tag{1.1}$$

where $\mathbf{P} = -i\hbar\nabla$ is the momentum operator,V is the general potential(??????? Defined in KS), m is the mass of electron and c is the speed of light, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are 4×4 matrices.

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I} & 0 \\ 0 & -\boldsymbol{I} \end{pmatrix} \tag{1.2}$$

where $\boldsymbol{I}$ is unit matrix, and $\boldsymbol{\sigma}$ is Pauli matrix.

$$\boldsymbol{\sigma} = (\boldsymbol{\sigma}_x\ \boldsymbol{\sigma}_y\ \boldsymbol{\sigma}_z) \tag{1.3}$$

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.4}$$

1.2 Derivation of scalar relativistic approximation and the spin orbit coupling

Ψ is the wave function of Hamiltonian 1.1, which has four components, but can be written with only two terms:

$$\Psi = \begin{pmatrix} \phi^{\uparrow} \\ \phi^{\downarrow} \\ \chi^{\uparrow} \\ \chi^{\downarrow} \end{pmatrix}, \Psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix} \tag{1.5}$$

where ϕ includes the two terms of $\phi^{\uparrow}$ and $\phi^{\downarrow}$, and χ contains $\chi^{\uparrow}$ and $\chi^{\downarrow}$; under the nonrelativistic limit,ϕ is bigger than χ by the ratio of v/c, where v and c are speed of particle and light, respectively, so the ϕ is the large term and χ is the small one.
In order to derive the scalar relativistic approximation and the spin-orbit coupling terms, we need to take use of the nonrelativistic limit approximation of the Dirac eigenvalue equation probelm, here nonrelativistic limit means $v^2/c^2 << 1$.

$$E\Psi = (c\boldsymbol{\alpha}\mathbf{P} + \boldsymbol{\beta}mc^2 + V)\Psi \tag{1.6}$$

For convenience, we define:

$$E' = E - mc^2 \tag{1.7}$$

where E is the total energy, mc^2 are E' are the rest mass energy and the remaining energy excluding the rest mass energy, under the nonrelativistic limit, E' is far smaller than mc^2. Now, putting equation 1.5 and 1.7 into equation 1.6:

$$\begin{aligned} &(E' - V)\Phi - c\boldsymbol{\sigma}\mathbf{P}\chi = 0 \\ &-c\boldsymbol{\sigma}\mathbf{P}\Phi + (E' + 2mc^2 - V)\chi = 0 \end{aligned} \tag{1.8}$$

To eliminate the χ (otherwise, it is the antiparticle problem), we can end up with the equation:

$$(V + \frac{1}{2m}(\boldsymbol{\sigma}\mathbf{P})(1 + \frac{E' - V}{2mc^2})^{-1}(\boldsymbol{\sigma}\mathbf{P}))\phi = E'\phi \tag{1.9}$$

Since $E' - V$ is far smaller than $2mc^2$, so taking advantage of the taylor expansion and the following identites:

$$\begin{aligned} &[\mathbf{P}, V] = -i\hbar\nabla V \\ &(\boldsymbol{\sigma}\mathbf{A})(\boldsymbol{\sigma}\mathbf{B}) = \mathbf{AB} + i\boldsymbol{\sigma}[\mathbf{A} \times \mathbf{B}] \end{aligned} \tag{1.10}$$

After some operations, we finally will get the following equation under the nonrelativistic limit:

$$E'\phi = (\frac{\mathbf{P}^2}{2m} + V - \frac{\mathbf{P}^4}{8m^3c^2} - \frac{i\hbar}{4m^2c^2}(\nabla V)\mathbf{P} + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}[\nabla V \times \mathbf{P}])\phi \tag{1.11}$$

Furthermore, we can approximate the above equation to the simpler expression under spherical symmetry potential:

$$E'\phi = (\frac{\mathbf{P}^2}{2m} + V - \frac{\mathbf{P}^4}{8m^3c^2} - \frac{i\hbar}{4m^2c^2}(\nabla V)\mathbf{P} + \frac{1}{2m^2c^2}\frac{1}{R}\frac{dV}{dR}\mathbf{SL})\phi \tag{1.12}$$

where $\mathbf{S} = \hbar\boldsymbol{\sigma}/2$ is the Pauli spinor, and $\mathbf{L} = \mathbf{R} \times \mathbf{P}$ is the orbital angular momentum operator. The terms of $\mathbf{P}^2/(2m) + V$ is Schrdinger term, $\mathbf{P}^4/(8m^3c^2)$ and $i\hbar(\nabla V)\mathbf{P}/(4m^2c^2)$ are the mass enhancement and Darwin term, respectively, both of them together is called the scalar relativistic approximation (SRA), the last term is the spin-orbit coupling(SOC) term.

1.3 Implementation of scalar relativistic approximation and spin-orbit coupling

In this section, we will focus on the implementation of scalar relativistic approximation and spin-orbit coupling in the Exciting Code, and we have to point out, the implementation is done only in the interstitial region(details see the introduction in the FP-LAPW method on page ???), the most important part from the implementation point is the matrix element, so first we will derive the matrix element of SRA, and then SOC, at last, we take use of different approaches to test the accuracy of the implementation.

1.3.1 Matrix element for the scalar relativistic approximation

To calculate the scalar relativistic approximation affect in the interstitial region, we need to fomulate matrix element of SRA, first we define the Hamiltonian of SRA:

$$\begin{aligned}\widehat{H}_{sra} &= -\frac{\mathbf{P}^4}{8m^3c^2} - \frac{i\hbar}{4m^2c^2}(\nabla V)\mathbf{P} \\ &= -\frac{\hbar^4\nabla^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}(\nabla V)\nabla\end{aligned} \tag{1.13}$$

In the atomic unit, we can simplify the above equation:

$$\widehat{H}_{sra} = -\frac{\nabla^4}{8c^2} - \frac{(\nabla V)\nabla}{4c^2} \tag{1.14}$$

The matrix element can be expressed:

$$
\begin{aligned}
H^{sra}_{G,G'} &= < \phi_G | \widehat{H}_{sra} | \phi_{G'} > \\
&= \frac{1}{\Omega} < e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} | -\frac{\nabla^4}{8c^2} - \frac{(\nabla V)\nabla}{4c^2} | e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}} > \\
&= \frac{1}{8c^2\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \{ -(k+G)^2(k+G')^2 - 2i(k+G') \sum_{\mathbf{G}''} V_{G''} i G'' e^{i\mathbf{G}''\mathbf{r}} \} \\
&= \frac{1}{8c^2\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \{ -(k+G)^2(k+G')^2 + 2(k+G') \sum_{\mathbf{G}''} V_{G''} G'' e^{i\mathbf{G}''\mathbf{r}} \}
\end{aligned}
\tag{1.15}
$$

Splitting two terms from the above equation, the first term is :

$$
\begin{aligned}
H^{sra}_1 &= \frac{1}{8c^2\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \{ -(k+G)^2(k+G')^2 \} \\
&= \frac{-(k+G)^2(k+G')^2}{8c^2} \frac{1}{\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}-\mathbf{G}')\mathbf{r}} \\
&= \frac{-(k+G)^2(k+G')^2}{8c^2} \frac{1}{\Omega} \int_\Omega d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} \theta_I(r) \\
&= \frac{-(k+G)^2(k+G')^2}{8c^2} \widetilde{\theta}_I(G-G')
\end{aligned}
\tag{1.16}
$$

where $\theta_I(r)$ is the characteristic function of the interstitial region (r included in MT, $\theta_I(r) = 0$, otherwise it is 1), $\widetilde{\theta}_I(r)$ comes from the Fourier transform of $\theta_I(r)$:

$$
\theta_I(r) = \sum_{\mathbf{G}} \widetilde{\theta}_I(G) e^{i\mathbf{G}\mathbf{r}} \tag{1.17}
$$

And

$$
\widetilde{\theta}_I(G) = \begin{cases} \delta_{G,0} - \sum_\alpha \frac{4\pi R^3_\alpha}{\Omega} \frac{j_1(|G|R_\alpha)}{|G|R_\alpha} e^{-iGr_\alpha} & \text{if } \mathbf{G} \leqslant \mathbf{G}_{max} \\ 0 & \text{if } \mathbf{G} > \mathbf{G}_{max} \end{cases}
$$

where R_α is the radius of the MT, r_α is the position refer to the αth atom, and j_1 is the *1*st order Bessel function.

The second term is:

$$
\begin{aligned}
H^{sra}_2 &= \frac{2(k+G')\sum_{\mathbf{G}''} V_{G''} G''}{8c^2\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{r}} e^{i\mathbf{G}''\mathbf{r}} \\
&= \frac{(k+G')\sum_{\mathbf{G}''} V_{G''} G''}{4c^2} \frac{1}{\Omega} \int_I d\mathbf{r} e^{i(\mathbf{G}'-\mathbf{G}+\mathbf{G}'')\mathbf{r}} \\
&= \frac{(k+G')\sum_{\mathbf{G}''} V_{G''} G''}{4c^2} \widetilde{\theta}_I(G-G'-G'')
\end{aligned}
\tag{1.18}
$$

So finally, after joining the equation 1.16 and 1.18 together, the final matrix element for the scalar relativistic approximation is:

$$
\begin{aligned}
H^{sra}_{G,G'} &= \frac{1}{8c^2} \{ -(k+G)^2(k+G')^2 \widetilde{\theta}_I(G-G') \\
&+ 2(k+G') \sum_{\mathbf{G}''} V_{G''} G'' \widetilde{\theta}_I(G-G'-G'') \}
\end{aligned}
\tag{1.19}
$$

1.3.2 Matrix element for the spin-orbit coupling

The spin-orbit coupling is included in second-variational scheme for the Exciting code, which means it takes use of the basis function which is expanded from the first variational wavefunction.

$$\begin{aligned} \widehat{H}_1\phi_1^i &= E_1^i\phi_1^i \\ (\widehat{H}_1 + \widehat{H}_{soc})\Psi &= E\Psi \end{aligned} \tag{1.20}$$

where $\widehat{H}_1$ and ϕ_1^i are first variational Hamiltonian and wave function, respectively, and $\Psi = \sum_i c_i\phi_1^i$. If multiply ϕ_1^j on the left side of the second item of the above equation.

$$< \phi_1^j|(\widehat{H}_1 + \widehat{H}_{soc})|\sum_i c_i\phi_1^i >= E < \phi_1^j|\sum_i c_i\phi_1^i > \tag{1.21}$$

After some operations, the above equation becomes:

$$\sum_i c_i\{E_1^i\delta_{i,j} + < \phi_1^j|\widehat{H}_{soc}|\phi_1^i >\} = \sum_i c_i E\delta_{i,j} \tag{1.22}$$

So finally, the above equation becomes the eigenvalue probelm $H_2C = EC$.

$$H_2 = \begin{bmatrix} E_1 + H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & E_2 + H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} & H_{N2} & \cdots & E_N + H_{NN} \end{bmatrix}, C = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix} \tag{1.23}$$

where $H_{j,i} =< \phi_1^j|\widehat{H}_{soc}|\phi_1^i >$. Actually, each block matrix of equation 1.28 is similar with above matrix for the implementation in the Exciting code,since there are spin up and spin down combinations.
To formulate the matrix element for SOC, first we define the Hamiltonian term of SOC:

$$\widehat{H}_{soc} = \frac{-i\hbar^2}{4m^2c^2}\boldsymbol{\sigma}[(\nabla V) \times \nabla] \tag{1.24}$$

Converting the above equation to atomic unit:

$$\widehat{H}_{soc} = \frac{-i}{4c^2}\boldsymbol{\sigma}[(\nabla V) \times \nabla] \tag{1.25}$$

Now calculate the matrix element:

$$
\begin{aligned}
H^{soc}_{j,j'} &= < \Psi_j | \widehat{H}_{soc} | \Psi_{j'} > \\
&= < \sum_{\mathbf{G}} c_{j,k+G} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} | \frac{-i}{4c^2} \boldsymbol{\sigma} [(\nabla V) \times \nabla] | \sum_{\mathbf{G}'} c_{j',k+G'} e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}} > \\
&= \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} < e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} | e^{i(\mathbf{k}+\mathbf{G}'+\mathbf{G}'')\mathbf{r}} \begin{pmatrix} h_z & h_x - ih_y \\ h_x + ih_y & -h_z \end{pmatrix} > \\
&= \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} \begin{pmatrix} h_z & h_x - ih_y \\ h_x + ih_y & -h_z \end{pmatrix} \int_I e^{i(\mathbf{G}'+\mathbf{G}''-\mathbf{G})\mathbf{r}} \\
&= \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} \begin{pmatrix} h_z & h_x - ih_y \\ h_x + ih_y & -h_z \end{pmatrix} \widetilde{\theta}_I (G - G' - G'')
\end{aligned}
\tag{1.26}
$$

where $c_{j,k+G}$ is the eigenvector from the first variational scheme, and h_x, h_y and h_z are the three components of the h:

$$
h = h(k, G', G'') = G'' \times (k + G') \tag{1.27}
$$

So in the subroutine of Exicting Code, the Hamiltonian is divided by the 2 $\times$ 2 matrix, each block of the matrix means the spin up and down combination matrix:

$$
\begin{pmatrix} \uparrow\uparrow & \uparrow\downarrow \\ \downarrow\uparrow & \downarrow\downarrow \end{pmatrix} \rightarrow \begin{pmatrix} h_z & h_x - ih_y \\ h_x + ih_y & -h_z \end{pmatrix} \tag{1.28}
$$

where $\downarrow$ and $\uparrow$ represent spin down and up, respectively. For example, when we calculate $\uparrow\uparrow$ part of the matrix,the equation 1.26 becomes:

$$
H^{soc}_{j,j'} = \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} h_z \widetilde{\theta}_I (G - G' - G'') \tag{1.29}
$$

If the $\downarrow\downarrow$ part of the matrix,the equation 1.26 becomes:

$$
H^{soc}_{j,j'} = \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} (-h_z) \widetilde{\theta}_I (G - G' - G'') \tag{1.30}
$$

If the $\uparrow\downarrow$ part of the matrix,the equation 1.26 becomes:

$$
H^{soc}_{j,j'} = \frac{i}{4c^2} \sum_{\mathbf{G},\mathbf{G}',\mathbf{G}''} c^*_{j,k+G} c_{j',k+G'} V_{G''} (h_x - ih_y) \widetilde{\theta}_I (G - G' - G'') \tag{1.31}
$$

1.4 Test of scalar relativistic approximation and spin-orbit coupling

In order to test the affect of SRA and SOC, It is not that easy job since the SOC and SRA is implemented in the IR, but still, we can search for some points to test the validity of SRA and SOC, in the next subsection, I will show the test from the different derivation and concrete example as well.

1.4.1 Test of matrix element for the scalar relativistic approximation

To test the SRA affect, I am still looking for concrete example from the application point, but from the theoretical point, I can use different mathmatical derivation to implement the code, and compare the accuracy.
So there is another point derivation from the SRA Hamiltonian , the equation 1.16 is still the same, but the second term:

$$\begin{aligned} H^2_{sra} &= \frac{1}{\Omega} < e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}| - \frac{(\nabla V(r))\nabla}{4c^2}|e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}} > \\ &= \frac{-1}{4c^2\Omega}\int_\Omega d\mathbf{r}e^{-i(k+G)}\{\theta_I(r)\nabla V(r)i(k+G')e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}}\} \\ &= \frac{-i(k+G')}{4c^2\Omega}\int_\Omega d\mathbf{r}e^{-i(k+G)}\{\theta_I(r)\nabla V(r)e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}}\} \end{aligned} \tag{1.32}$$

In the above equation, we take advantage of the Fourier transform:

$$\theta_I(r)\nabla V(r) = \sum_{\mathbf{G}''}\widetilde{V}_{G''}e^{i\mathbf{G}''\mathbf{r}} \tag{1.33}$$

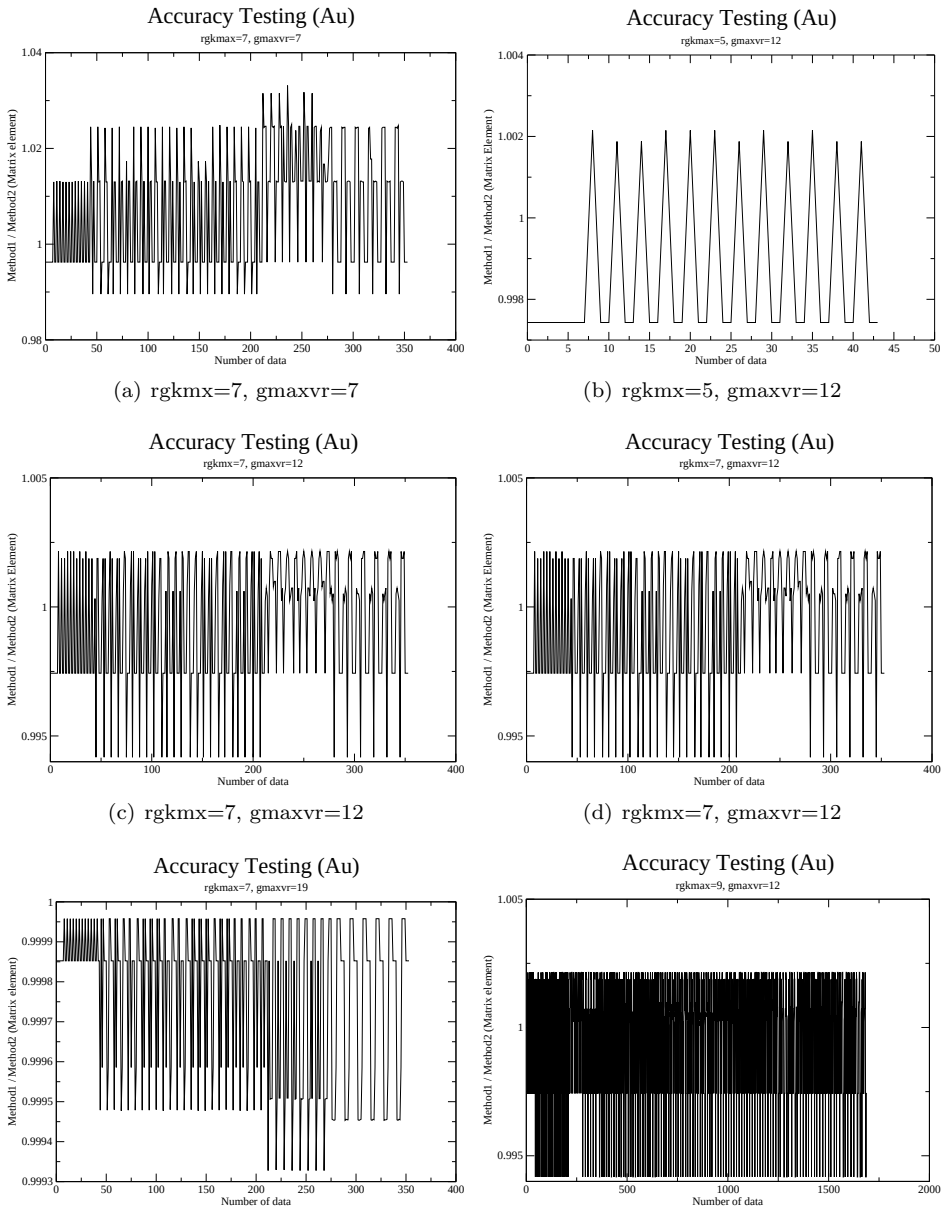
Then the equation 1.32 will change to :

$$\begin{aligned} H^{sra}_2 &== \frac{-i(k+G')}{4c^2\Omega}\int_\Omega d\mathbf{r}e^{-i(k+G)}\{\theta_I(r)\nabla V(r)e^{i(\mathbf{k}+\mathbf{G}')\mathbf{r}}\} \\ &= \frac{-i(k+G')}{4c^2\Omega}\int_\Omega d\mathbf{r}\sum_{\mathbf{G}''}\widetilde{V}_{G''}e^{i(G'-G+G'')} \\ &= \frac{-i(k+G')}{4c^2}\sum_{\mathbf{G}''}\widetilde{V}_{G''}\delta_{G'',G-G'} \\ &= \frac{-i(k+G')}{4c^2}\widetilde{V}_{G-G'} \end{aligned} \tag{1.34}$$

So finally, we get the final equation:

$$H^{sra}_{G,G'} = \frac{-(k+G)^2(k+G')^2}{8c^2}\widetilde{\theta}_I(G-G') + \frac{-i(k+G')}{4c^2}\widetilde{V}_{G-G'} \tag{1.35}$$

Comparing equation 1.19 with equation 1.35, actually, the code will get more performance when using the equation 1.35 since the G'' normally is in the order of 10^4 to 10^5.
Now we compare these two methods with the calculated matrix element value.



(a) rgkmx=7, gmaxvr=7

(b) rgkmx=5, gmaxvr=12

(c) rgkmx=7, gmaxvr=12

(d) rgkmx=7, gmaxvr=12

(e) rgkmx=7, gmaxvr=19

(f) rgkmx=9, gmaxvr=12

Figure 1.1: Accuracy testing for Au, the left column is under the condition fixing the rgkmax value but gmaxvr varys. right column is oppsite. Only the matrix element value great than 1E-6 are plotted, and all the imaginary part of value are less than 1E-6, so the imaginary part does not plot in the above figure, for the Y-axis, the Method1 means using equation 1.34, and Method2 means using equation 1.18.And the data comes from the first k point during the first self-consistent process.

From the above figure, first we notice both of them generate the similar result within certain range of difference, so the implementation is correct, then we can check how important parameter affect the result. With the default number of $gmaxvr$ and $rgkmax$ by the Exciting code ($gmaxvr$=12, $rgkmax$=7), the accuracy is controlled under 0.5%, here,$gmaxvr$ means maximum length of G for expanding the interstitial density and potential and $rgkmax$ will control the number of basis funtion. but when reducing the number $gmaxvr$ to 7,the accuracy is down to 2% to 3%.However increasing the number of $rgkmax$, the acccuracy is not improve that much, which means the accuracy is quite controlled by the number of $gmaxvr$. Actually, we choose the equation 1.34 to implement this SRA affect, because the code will gain more performance than using equation 1.18 under the reasonable number of $gmaxvr$.

1.4.2 Test of matrix element for the spin-orbit coupling

In this section, we first show another derivation of SOC, and then compare the matrix element result like previous section, at last, we will show one concrete example which is affected by the SOC.

$$\begin{aligned} H^{soc}_{j,j'} &=< \Psi_j(r)|\widehat{H}_{soc}|\Psi_{j'}(r) > \\ &=< \Psi_j(r)|\frac{-i}{4c^2}\boldsymbol{\sigma}[(\nabla V(r)) \times \nabla]|\Psi_{j'}(r) > \\ &= \frac{-i}{4c^2}\int_\Omega \Psi^*_j(r)\theta_I(r)\boldsymbol{\sigma}\{\nabla V(r)\} \times \{\nabla\Psi_{j'}(r)\} > \end{aligned} \tag{1.36}$$

In the above equation, we can use the Fourier transform for each block of following equaion (like equation 1.29 to 1.31):

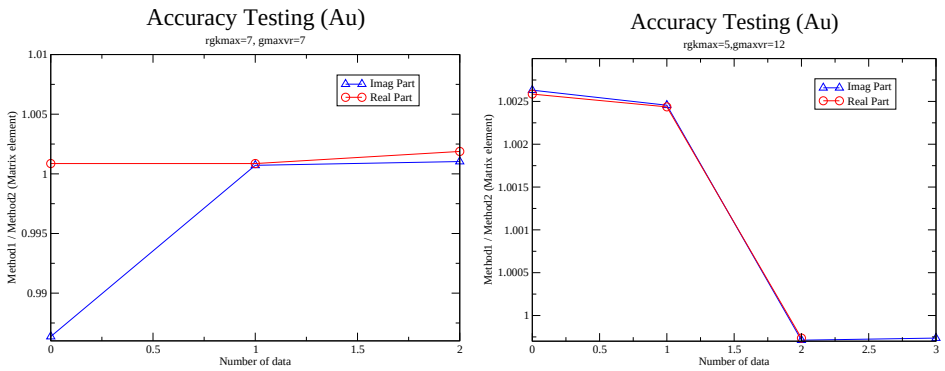
$$\boldsymbol{\sigma}\theta_I(r)\{\nabla V(r)\} \times \{\nabla\Psi_{j'}(r)\} = f(r) = \sum_{\mathbf{G'}} c_{j',k+G'}e^{i(\mathbf{k}+\mathbf{G'})\mathbf{r}} \tag{1.37}$$

So if we define $\Psi^{ft}_{j'}(r) = \sum_{\mathbf{G'}} c_{j',k+G'}e^{i(\mathbf{k}+\mathbf{G'})\mathbf{r}}$ we can write down the equation 1.36:

$$\begin{aligned} H^{soc}_{j,j'} &= \frac{-i}{4c^2}\int_\Omega \Psi^*_j(r)\Psi^{ft}_{j'}(r) > \\ &= \frac{-i}{4c^2}\int_\Omega \Psi^*_j(r)\Psi^{fs}_{j'}(r) \\ &= \frac{-i}{4c^2}\sum_{\mathbf{G}} c^*_{j,k+G}c_{j',k+G} \end{aligned} \tag{1.38}$$

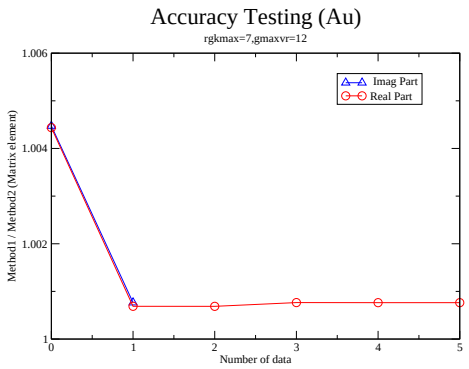
Comparing the above equation 1.38 with 1.26, we can clear see that the equation 1.38 is much simplier and better performance, so in the implementaion we take advantage of the equation 1.38, but using 1.26 for testing the accuracy even though it is quite time consuming (for each matrix element there are three loops, so if each loop in the order of 10^2, then it is up to the order of 10^6), so in the implementaion, we use equation 1.38.

Now let us examinate these two methods:

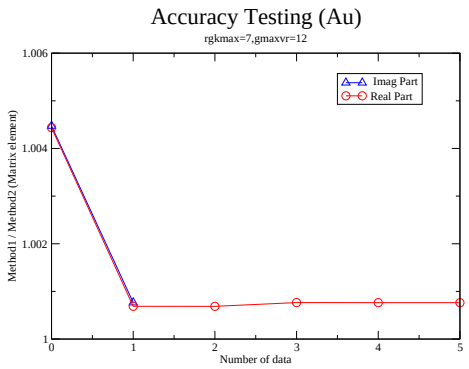


(a) rgkmx=7, gmaxvr=7

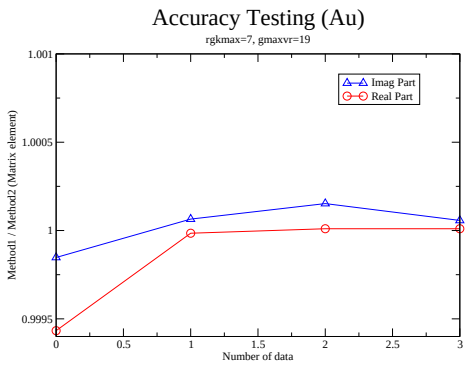
(b) rgkmx=5, gmaxvr=12



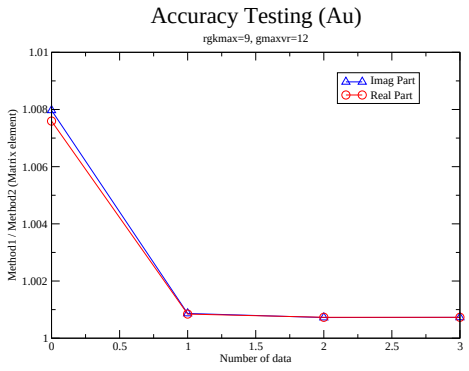
(c) rgkmx=7, gmaxvr=12



(d) rgkmx=7, gmaxvr=12



(e) rgkmx=7, gmaxvr=19



(f) rgkmx=9, gmaxvr=12

Figure 1.2: Accuracy testing for Au, the left column is under the condition fixing the rgkmax value but gmaxvr varys. right column is oppsite.Only the matrix element value great than 1E-6 are plotted, for the Y-axis, the Method1 means using equation 1.38, and Method2 means using equation 1.26.And the data comes from the first k point during the first self-consistent process.

From the above figure, we can see both of the methods (equation 1.38 and 1.26) have the similar result, so the implementation is correct, and then it

is quite apparently there are less number of data, which means the second variational method is quite efficient.

We can check that with the default number of $gmaxvr$ and $rgkmax$ by the Exciting code ($gmaxvr$=12, $rgkmax$=7), the accuracy is controlled under 0.5%, but when reducing or incresing the number $gmaxvr$ to 7 or 9, the accuracy is down to 1% or 0.05%. However, with the varys of $rgkmax$, the accuracy is not change that much.

Let us see the SOC affect on the Dirac point of Graphene, in the case of without spin polarization, there is no splitting energy on the Dirac point, however, in the previous researchers' calculation, there are splitting energy on the Dirac point considering the SOC only in the MT, which is in the order of 20 μEv,but since there is no researchers done the calculation with the SOC contribution on the MT+IR,so I use the implementaion to calculate it, in these calculations, I calculate SOC affect in different radius in MT and MT+IR, then means the SOC in IR as well.

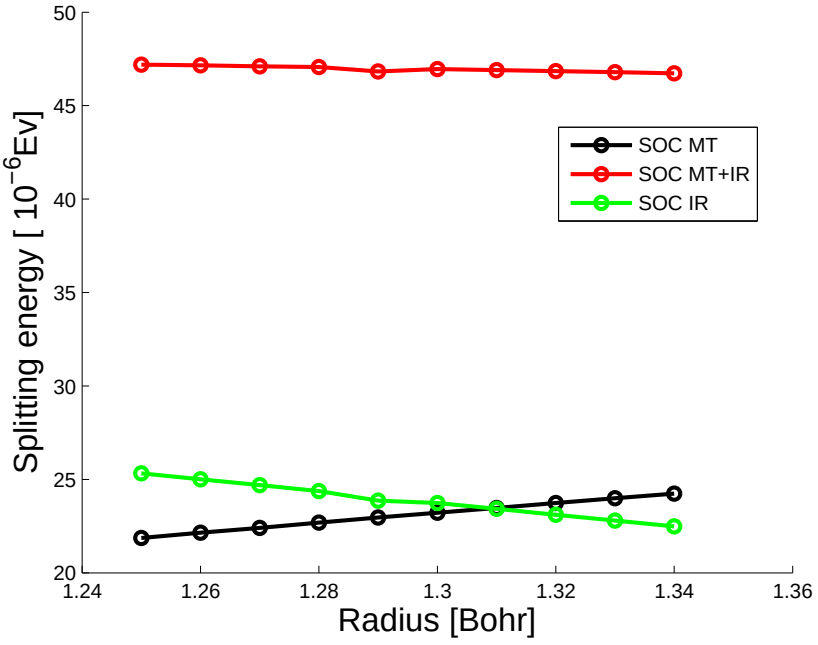


Figure 1.3: Spin-orbit coupling contribution for Graphene

From the above figure, we can clear see with the increasing of MT radius, the contribution from SOC in MT increases, but oppsite for SOC in IR, since the whole space is contributed by SOC (MT+IR) now, so the total contribute is stable with the varys of MT radius. Also there is one very intriguing phenomenon, the SOC intribution is in the same order either in the MT or IR,however, it is believed in the order 20 μEv before, but from our calculation,actually it is double since the contribution from IR is ignored from all the previous calculation result.