Ab Initio Elastic Properties calculation of Gold (Au)

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Abstract. Elastic properties of Gold (Au) are calculated based on Ab Initio approach by which total energy of Au in respect with volume can be obtained. The elastic properties can then be determined by fitting the calculation results with particular parametric formula. Compared with experimental data (macroscopic properties), it is found that the use of Local Density Approximation (LDA) as exchange-correlation functional in calculation produce good results than Generalized Gradient Approximation (GGA) based. Hence, Ab Initio approach is potential to predict elastic properties of solid. However, the exchange-correlation functional should be chosen with great care. This calculation approach is useful for multi-scale simulation which link the result from micro-macroscopic properties and vice versa where engineering can benefit from such a framework.

1. Introduction
Gold has versatility and unique properties which make it indispensable in engineering and electronic apart from its role in economy. It is found that the gold applications are ranging from catalyst [1], medical implant [2,3], catalytic converter [4], wire and microchip [5] etc. For applications in which the mechanical response needs to be determined, elastic properties are of importance to deal with. Hence, the mechanical behavior of structures is feasible to be predicted once the elastics parameters are available.

Traditionally, the mechanical properties are investigated based on phenomenological and empirical concept where some measurement standard [6,7,8,9] are employed to obtain the properties. However, this is not always good option particularly for wide range variation and specification of material as this can be costly. This motivates the use of numerical method in predicting mechanical properties of material. Moreover, this becomes expanding considering the recent advances in computer hardware and software from which the computer simulation in material science delivering many useful insight.

In general, the material properties can be predicted using Density Functional Theory (DFT) under ground-state condition. The main idea of DFT is that energy of an electronic system can be determined by electron density as suggested by Fermi in 1929. This idea becomes realistic after Hohenberg-Kohn [10] and Kohn-sham [11] gave the exact relationship between electron density and energy.

In this research the DFT is used for calculating the elastic properties of gold (Au). Despite the elastic properties related with temperature, the result under ground-state condition is expected still
relevant as the temperature effect on elastic properties is small for many materials at room temperature. The elastic properties obtained can be further used to calculate vibration response of typical structure particularly gold bar that is useful to support our research in developing gold purity testing [12].

The outline of this paper is as follows. Section 2 summarizes the Density Functional Theory (DFT). Section 3 shows the calculation procedure for determining elastic constants particularly related with the bulk modulus. Section 4 describes the implementation of DFT including the set of parameters used in the calculation. The results are presented in Section 5 while section 6 contains some conclusions which can be drawn from this research.

2. Density Functional Theory (DFT)

The ground-state energy of an electron system is calculated by searching through possible electronic densities \( n(\mathbf{r}) \) until some minimum energy \( E \) is found. According to Kohn and Sham [11], the electron density \( n(\mathbf{r}) \) can be formed from single-electron orbitals where each orbital is eigenstates of a local potential. The total energy of solid can then be written as

\[
E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + E_H[n(\mathbf{r})] + U_{\text{ex}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})] + E_{\text{ion}}
\]

where \( n(\mathbf{r}) = \sum \phi(\mathbf{r}) \) is the density of electron in the solid, \( \phi(\mathbf{r}) \) are the occupied single-particle states. Meanwhile, \( T_0[n(\mathbf{r})] \) is the kinetic energy of a non-interacting set of electrons of density \( n(\mathbf{r}) \), \( E_H[n(\mathbf{r})] \) is the self-coulomb interaction of the electron density, \( U_{\text{ex}}[n(\mathbf{r})] \) is the interaction between the electron and the Coulomb field of the nuclei, \( E_{\text{xc}}[n(\mathbf{r})] \) is the exchange-correlation energy of the electrons, and \( E_{\text{ion}} \) is the Coulomb interaction between the bare nuclei.

All terms in Eq. (1) are actually exact calculation except the terms \( T_0[n(\mathbf{r})] \) and \( E_{\text{xc}}[n(\mathbf{r})] \) have not been exactly determined. For this, an approximation is used where the simplest approach can be realized by considering \( E_{\text{xc}}[n(\mathbf{r})] \) only dependent on the local electron density. Such approximation is known as Local Density Approximation (LDA). The LDA usually gives very good results for system with slowly varying densities and over-binds molecules and solid. However, LDA produces considerable error for weakly bonded system.

To deal with the shortcoming of LDA, the approximation can include gradient correction to electron density in order to provide more physical information. This kind of approximation is known as Generalized Gradient Approximation (GGA). In nature, this approximation will be able to produce better results for most things particularly a less-dense system.

3. Calculation of elastic constant

The matrix of elastic constant \( C \) in most general form has 81 components. The presence of symmetrical form of stress and strain reduces the component to 36 independent elastic constant. The number of the elastic constant further decreases when additional symmetry arguments introduced by the crystal lattice. In particular, for the case of a cubic lattice, it has been found that \( C_{11} = C_{22} = C_{33} \), \( C_{12} = C_{23} = C_{32} = C_{13} = C_{31} \), \( C_{44} = C_{55} = C_{66} \) considering the \( x \), \( y \) and \( z \) are identical by symmetry. Moreover, the corresponding off diagonal shear component \( C_{45} = C_{54} = C_{65} = C_{56} = C_{64} \) is equal to zero while \( C_{14} = C_{41} = \ldots = 0 \) indicating none of mixed compression/shear coupling is present. Hence, only three independent elastic constants i.e. \( c_{11} \), \( c_{12} \) and \( c_{44} \) are remain with the explicit form of tensor reduced to
The total change in energy can be expressed by means of Taylor expansion as follows

$$E(V, \delta) = E(V_0, 0) + V_0 \left( \sum_{i=1}^{6} c_{ij} \delta_i + \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij} \delta_i \delta_j + O(\delta^3) \right)$$  \hspace{1cm} (3)$$

where $\delta$ and $\tau$ is the strain on the crystal, $C_{ij}$ are the elastic constants and $V_0$ is the volume of unstrained cubic system at which the elastic constants are evaluated. For more convenient way, Voigt notation can be used to replace $xx = 1, yy = 2, zz = 3, yz = 4, zx = 5$ and $xy = 6$ as index of elastic constant in tensor.

The elastic moduli of cubic crystal related with the bulk modulus $B$ can be obtained using

$$B = \frac{(C_{11} + 2C_{12})}{3}$$  \hspace{1cm} (4)$$

which can be obtained by introducing some strain $\delta$ to distort primitive vectors and relax all internal parameters in order to minimize the total energy using the following strain tensor

$$D = \begin{bmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 + \delta \end{bmatrix}$$  \hspace{1cm} (5)$$

It is customary to used several volumes that is within 10-20% of expected equilibrium volume until the minimum is found within this range. If this is not the case, the range need to be extended until the minimum bracketed is obtained.

In principle, Eq. (1) self-consistently is to be solved. It would be stopped when an accurate total energy in Eq. (1) and charge density have been found. The internal lattice parameter will be fixed once the volume of the system has been specified. A set of total energy $E_i = E(V_i)$ can thus be determined where the bulk modulus is related to the curvature of $E(V_i)$.

The resulting set $(V_i, E_i)$ is fit to third order polynomial as follows

$$E(V) = p_1 V^1 + p_2 V^2 + p_3 V + p_4$$  \hspace{1cm} (6)$$

so that $p_1, p_2, p_3,$ and $p_4$ can be obtained. From this, initial values related with parameters $E_0, V_0, B_0$ and $B'_0$ can be determined using following expression

$$V_0 = \frac{\partial E}{\partial V} = 0$$  \hspace{1cm} (7)$$

$$E_0 = p_1 V_0^1 + p_2 V_0^2 + p_3 V_0 + p_4$$  \hspace{1cm} (8)$$

$$B_0 = \frac{\partial^2 E}{\partial V^2} = V_0 (6p_1 V_0 + 2p_2)$$  \hspace{1cm} (9)$$

where $E_0, V_0, B_0$ and $B'_0$ are respectively the equilibrium energy, equilibrium volume, bulk modulus and pressure derivative of the bulk modulus. Meanwhile, $B'_0$ is usually around 2. The optimal $E_0, V_0,$
$B_0$ and $B'_0$ are calculated iteratively with minimum error using a least square fit of the set $(V_i, E_i)$ that fits to equation of state proposed Birc-Murnaghan [13] as follows

$$E_{\text{fit}}(V) = E_0 + \frac{9V_0B_0}{16}\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^{\frac{3}{2}}B'_0 + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left(6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right)$$

(10)

4. Calculation Method

Calculation has been performed using Density Functional Theory (DFT) calculation based on Kohn-Sham formulation [11] as implemented in Quantum Espresso Package. Local Density Approximation (LDA) was used as exchange –correlation functional. For comparison purpose, the Generalized Gradient Approximation (GGA) proposed by Pardew-Wang 91[14] was also used. The basis set expand in terms of plane wave with energy cut-off at 50 Ry. Regarding to core electrons, the ultra-soft pseudopotential was used. The integration in Brillouin zone was done on 31 x 31 x 31 grid sampled by Monkhorst-pack method [15]. This was sufficient in the sense that the predicted elastic properties remain unchanged when the dense $k$ mesh was increased. Moreover, one Au primitive cell is FCC-lattice was used to represent Au bulk.

5. Results

Energy total as results of DFT calculation can be observed from Fig.1. It is clear that the use of exchange energy potential LDA dan GGA produce different results. Generally, it is clear that the DFT calculation using GGA have higher energy total for similar volume range while that of LDA is overbinding. Moreover, the equilibrium energy $E_0$ associated with volume $V_0$ is pronounced at higher volume.

![Figure 1.](image-url)

**Figure 1.** Total energy $E$ of Au calculated using DFT LDA indicated by blue square and DFT GGA indicated by red dotted. Those data are fitted with Birch-Murnaghan equation of state.

This tendency is supported by curve fitting results, using Birch-Murnaghan equation of state, as listed in Table1. It is found that the DFT calculation using LDA gives $E_0$ is equal -4.45 eV
associated with $V_0$ of 16.37 Å³ while that of GGA is -3.20 eV and $V_0$ of 18.16 Å³. From this parameter, the bulk modulus is found to be 195.51 GPa and 137.99 GPa for LDA dan GGA respectively. Meanwhile, according to experimental results the bulk modulus $B_0$ of Au is 220 GPa [16]. Compared with the experimental result, this gives error of 11.13% and 37.28% for LDA and GGA respectively. Hence, the bulk modulus calculated using LDA as exchange-correlation functional is quite good in agreement than that of GGA.

| Parameters | LDA  | GGA  |
|------------|------|------|
| $V_0$      | 16.37| 18.16|
| $E_0$      | -4.45| -3.20|
| $B_0$      | 195.51| 137.99|
| $B'_0$     | 5.67 | 5.98 |

Table 1. Fitting parameters comparison between LDA result and GGA one

6. Conclusions
DFT calculation has been used to calculate the bulk modulus $B_0$ of gold Au. It is found that the bulk modulus of Au is 195.51 for DFT calculation using LDA as exchange energy potential. This result is in quite good agreement with the experimental result where the bulk modulus of Au is around 220 GPa. Meanwhile, greater error in predicting bulk modulus is found for DFT calculation using GGA. Therefore, the DFT calculation is potential to use to predict the elastic properties of material but the exchange-correlation functional should be chosen with a great care as more physical exchange-correlation functional does not always offer a better result. From practical purpose, this result can be useful for multi-scale simulation which link the result from micro-macroscopic properties and vice versa.

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