EQUATION OF STATE BASED ON THE RYDBERG POTENTIAL

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Abstract

A method has been developed to obtain an equation of state using an interatomic potential function. We have used the Rydberg potential function to obtain expressions for pressure and bulk modulus. Discussions and conclusions are also presented.

Keywords: Rydberg potential function, Equation of state, bulk modulus, pressure derivatives, Lagrangian strain.

INTRODUCTION

The first quantum – based potential to receive serious attention was due to Morse [1].

$$\phi = A\left\{\exp\left[2f\left(1-\frac{r}{a}\right)\right]-2\exp\left[f\left(1-\frac{r}{a}\right)\right]\right\} \tag{1}$$

where ϕ is the potential energy expressed as a function of interatomic distance r, A, f and a are the potential parameter which remain constant for a given solid. It arose originally from a study of molecular spectroscopy but was used in a finite strain theory by Slater [2]. The Morse potential was, for many years, the most favored equation for equation-of-state studies but has been displaced in popularity by another potential published shortly after Morse's work by Rydberg [3].

$$\phi = A\left[1-f\left(1-\frac{r}{a}\right)\right]\exp\left[f\left(1-\frac{r}{a}\right)\right] \tag{2}$$

Rydberg was also working on molecular spectra and concluded that equation (2) gave a better fit to the vibrational spectrum of H_2 than did equation(1). Equation (2) gives

$$P(x) = 3K_0(1-x)x^{-2}\exp\left[\frac{3}{2}(K_0'-1)(1-x)\right] \tag{3}$$

where $x=(V/V_0)^{1/3}$, K_0 and K_0' are the isothermal bulk modulus and isothermal bulk modulus pressure derivative at zero pressure. The expressions for K, K', KK'' and K^2K''' obtained from the above EOS are given below

$$K = -K_0\left[-2x^{-2}+x^{-1}\left\{1-\left(\frac{3}{2}(K_0'-1)\right)\right\}+\left(\frac{3}{2}(K_0'-1)\right)\right]\exp\left[\left\{\frac{3}{2}(K_0'-1)\right\}(1-x)\right] \tag{4}$$

$$K' = \frac{K_0}{3K}\left[4x^{-2} + x^{-1}\left\{3\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right\} - \left\{\frac{3}{2}(K'_0 - 1)\right\}\right.$$

$$\left. + \left\{\frac{3}{2}(K'_0 - 1)\right\}^2 - x\left\{\frac{3}{2}(K'_0 - 1)\right\}^2\right]\exp\left[\left\{\frac{3}{2}(K'_0 - 1)\right\}(1 - x)\right] \tag{5}$$

$$KK'' = -\frac{K_0}{9K}\left[-8x^{-2} - x^{-1}\left\{7\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right\} - \left\{3\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right\}\left(\frac{3}{2}(K'_0 - 1)\right)\right.$$

$$\left. - x\left\{\frac{3}{2}(K'_0 - 1)\right\}^3 + x^2\left\{\frac{3}{2}(K'_0 - 1)\right\}^3\right]\exp\left[\left\{\frac{3}{2}(K'_0 - 1)\right\}(1 - x)\right] - K'^2 \tag{6}$$

$$K^2K''' = \frac{K_0}{27K}\left[A_1x^{-2} + A_2x^{-1} + A_3 + A_4x + A_5x^2 - A_6x^3\right]$$

$$\exp\left[\left\{\frac{3}{2}(K'_0 - 1)\right\}(1 - x)\right] - 4KK''K' - K'^3 \tag{7}$$

$$A_1 = 16 \tag{8}$$

$$A_2 = \left[15\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right] \tag{9}$$

$$A_3 = \left(\frac{3}{2}(K'_0 - 1)\right)\left[7\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right] \tag{10}$$

$$A_4 = \left(\frac{3}{2}(K'_0 - 1)\right)^2\left[2\left(\frac{3}{2}(K'_0 - 1)\right) - 1\right] \tag{11}$$

$$A_5 = \left(\frac{3}{2}(K'_0 - 1)\right)^3\left[2 + \left(\frac{3}{2}(K'_0 - 1)\right)\right] \tag{12}$$

$$A_6 = \left(\frac{3}{2}(K'_0 - 1)\right)^4 \tag{13}$$

Vocadlo [4, 5] performed, ab initio electronic structure pseudopotential calculations on the hexagonal close-packed phase of iron at a number of fixed volumes. A pressure – volume data set was produced in order to text different EOS such as the Birch – Murnaghan

EOS [6, 7], the logarithmic EOS [8] and the Rydberg – Vinet EOS [9, 10]. He found that the logarithmic EOS (fourth order) and the Rydberg – Vinet EOS give a far better representation of compressional behavior than the other EOS which are frequently found in the literature. It should be mentioned that an EOS was obtained by Vinet et al. [9] using the potential function

$$\phi(r) = -\Delta\phi(1 + a^*)\exp[-a^*] \tag{14}$$

with $a^* = \frac{r - r_0}{l}$

where $\Delta\phi$ is the binding energy, and r is the length per electron. It turned out that equation is identical with the Rydberg potential function and therefore EOS determined by Vinet et al. is more appropriately designats as the Rydberg – Vinet EOS. The superiority of the Rydberg – Vinet EOS is shown by Schlosser and Ferrante [11] comparing various EOSs for K/K_0 with the experimental data.

The shortcomings of the Birch-Murnaghan EOS formulations have also been pointed out by Stacey and Davis [12]. In fact at high compressions the third order as well the fourth order Birch – Murnaghan EOS becomes inadequate to predict pressure – volume data for different solids [13] and for the Earth interior [12]. Hama and Suito [13] have shown that the Rydberg – Vinet EOS is supreme among the others and predicts both the pressure and the bulk modulus correctly up to 10TPa for monatomic solids and up to 1TPa for diatomic solids.

Cohen [14] has discussed the reasons for the accuracy of the most-used formulation, based on the Birch EOS [15] and compared with the Rydberg – Vinet EOS [9]. Jeanloz [16] has also shown that the Birch EOS and the Rydberg – Vinet EOS can be similar up to moderate compressions. He shows that this breaks down at high compressions and for highly compressible materials the Rydberg-Vinet EOS is considerably more accurate. A logarithmic EOS [8] and another exponential EOS [17] have been discussed and compared with the Rydberg – Vinet and the Birch EOSs. Finally, Cohen has shown how subtle transitions can be detected by deviations from an EOS. Hemley et al. [18] has shown in analysis of X-ray diffraction data for hydrogen that the Rydberg-Vinet EOS is considerably more accurate than the Birch equation. Cohen [14] has obtained the theoretical results for the E vs V in case of the using the first – principles method based on the linerarized augmented plane wave (LAPW) [19] and local density approximation (LDA) [20]. The E vs V results were also calculated using different EOS such as the Rydberg-Vinet EOS and the Birch EOS. Comparision of these results with those based on the first-principles demonstrated that the Rydberg-Vinet EOS gives better result than the Birch EOS. He has also shown results for the fourth-order Birch EOS, which inspite of an additional parameter, is still not as good as the Rydberg-Vinet EOS. As more parameters are added, the quality of the fit improves, but the correlations among individual parameters increases. He has considered EOSs of two stiff metals, Ta and Pt. Energies were computed using the LAPW method and the generalized gradient approximation [21]. The Rydberg – Vinet EOS fits better than the Birch EOS for Pt, but for Ta the Birch EOS fits better.

The Rydberg-Vinet EOS has been widely used in the field of condensed matter physics and geophysics. It went unnoticed for many years that the Rydberg-EOS and the Vinet EOS are one and the same equation. This fact was disclosed by Stacey [22] for the first time and later discussed in some detail by Gaurav [23] and Arunesh [24]. Recently, attention has been drawn [23, 25] on the Rydberg – Vinet EOS and the Shanker EOS [26], which yield results very close to each other for different types of solids up to very high pressures. Sushil [27] has calculated the thermodynamics parameters for solids. The input data used in his calculation for these parameters are taken from Hama and Suito [13]. He were also calculated these parameters from different EOSs. The results obtained from the EOS based on the Lagrangian strain deviate much from those derived from other equations. This is due to the poor convergence of the free energy expansion in terms of the Lagrangian strain [12, 27]. The results obtained from the Birch – Murnaghan fourth – orders EOS [28] are in fair agreement with those based on the other equations.

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