

Application of the Biswas-Hamann Parameters for Describing the Kaxiras-Pandey Bond Energy

Teik-Cheng Lim

School of Science and Technology, SIM University (UniSIM),
461 Clementi Road, S 599491, Republic of Singapore.

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Abstract:

The 2-body interaction energy according to the Biswas-Hamann potential has a longer history than that of the Kaxiras-Pandey potential. Accordingly, covalent bond stretching energy for the former has been parameterized more than that of the latter. This paper enables a cost-effective and time-saving approach for extracting parameters of the newer potential from those of the older potential. This paper adopts a simultaneous imposition of equal force constant and equal energy integral for relating parameters from both potentials. Plotted results reveal very good agreement. Due to the high cost involved in spectroscopic experimentation and *ab initio* supercomputing, the availability of parameter conversion would be a good alternative for computational chemistry modeling.

1. Introduction

With increasing investigation into various silicon nanodevices (e.g. [1-3]) and their applications thereof, the importance of solid state interatomic many-body modeling should not be overlooked. Empirical many-body potential functions would serve well the computational requirements of these silicon nanodevices due to their ease of computation. These empirical potential functions have been developed for silicon by Biswas and Hamann [4], Kaxiras and Pandey [5] and many others. Reviews on the various potential functions for solid state systems of Si, C and other systems have been made by Stoneham et al. [6], Balamane et al. [7], Erkoç [8] and Sathyamurthy [9]. Relationships between various potential energy functions have been established for small deformation [10-13] and for large deformation [14-17]. The former was attained by imposing equal force constant while the latter by means of equating equal energy integral from equilibrium bond length to bond dissociation. These parameter relationships are useful whenever a computational application's user prefers a set of parameters in a particular potential function over the incorporated potential function in the software. The two methods of potential function conversions, however, encounter limitations. The method by force constant equates equal potential energy curvature at the well-depth's minimum, thereby enabling impeccable agreement for small deformation but significant discrepancies are normally observed for $r > 1.2R$. The method by energy integral ensures equal area of energy versus bond length within $R \leq r \leq \infty$ such that the relaxation of equal curvature at the well-depth minimum leads to significant discrepancies in large bond compression. This paper combines both methods to develop parameter conversion that is accurate for (i) large bond compression ($0 < r < R$), (ii) small bond deformation ($r \cong R$), and (iii) large bond stretching ($r > R$).

2. Analysis

The 2-body energy portion of the Biswas-Hamann [4] and Kaxiras-Pandey [5] potentials are given as

$$U_{BH} = A_{BH1} \exp(-\lambda_1 r) + A_{BH2} \exp(-\lambda_2 r) \quad (1)$$

and

$$U_{KP} = A_{KP1} \exp(-\alpha_1 r^2) - A_{KP2} \exp(-\alpha_2 r^2) \quad (2)$$

respectively, with A_{BH2} being negative [4]. To pave a way for both functions to be related, these 4-parameter potentials are expressed in a more common form that consists of dissociation energy, D , and the equilibrium bond length, R . In this way both functions can be reduced into 2-parameter potentials only when expressed in non-dimensionalized forms, i.e.

$$\frac{U_{BH}}{D} = f_{BH} \left(\lambda_1, \lambda_2, \frac{r}{R} \right) \quad (3)$$

and

$$\frac{U_{KP}}{D} = f_{KP} \left(\alpha_1, \alpha_2, \frac{r}{R} \right). \quad (4)$$

Specifically, imposing

$$\left(\frac{\partial U_{BH}}{\partial r} \right)_{r=R} = \left(\frac{\partial U_{KP}}{\partial r} \right)_{r=R} = 0 \quad (5)$$

and

$$(U_{BH})_{r=R} = (U_{KP})_{r=R} = -D \quad (6)$$

on Eqs.(1) and (2) leads to

$$\frac{U_{BH}}{D} = \frac{\lambda_2}{\lambda_1 - \lambda_2} \exp \left[\lambda_1 R \left(1 - \frac{r}{R} \right) \right] - \frac{\lambda_1}{\lambda_1 - \lambda_2} \exp \left[\lambda_2 R \left(1 - \frac{r}{R} \right) \right] \quad (7)$$

and

$$\frac{U_{KP}}{D} = \frac{\alpha_2}{\alpha_1 - \alpha_2} \exp \left[\alpha_1 R^2 \left(1 - \frac{r^2}{R^2} \right) \right] - \frac{\alpha_1}{\alpha_1 - \alpha_2} \exp \left[\alpha_2 R^2 \left(1 - \frac{r^2}{R^2} \right) \right] \quad (8)$$

respectively, whereby the equilibrium bond length is

$$R = \frac{1}{\lambda_1 - \lambda_2} \ln \left(-\frac{\lambda_1 A_{BH1}}{\lambda_2 A_{BH2}} \right) \quad (9)$$

in terms of Biswas-Hamann parameters, and

$$R = \sqrt{\frac{1}{\alpha_1 - \alpha_2} \ln \left(\frac{\alpha_1 A_{KP1}}{\alpha_2 A_{KP2}} \right)} \quad (10)$$

in terms of Kaxiras-Pandey parameters by means of Eq.(5). The bond dissociation energy can be expressed as

$$D = -A_{BH1} \exp \left[-\frac{\lambda_1}{\lambda_1 - \lambda_2} \ln \left(-\frac{\lambda_1 A_{BH1}}{\lambda_2 A_{BH2}} \right) \right] - A_{BH2} \exp \left[-\frac{\lambda_2}{\lambda_1 - \lambda_2} \ln \left(-\frac{\lambda_1 A_{BH1}}{\lambda_2 A_{BH2}} \right) \right] \quad (11)$$

in terms of Biswas-Hamann parameters, and

$$D = -A_{KP1} \exp \left[-\frac{\alpha_1}{\alpha_1 - \alpha_2} \ln \left(-\frac{\alpha_1 A_{KP1}}{\alpha_2 A_{KP2}} \right) \right] + A_{KP2} \exp \left[-\frac{\alpha_2}{\alpha_1 - \alpha_2} \ln \left(-\frac{\alpha_1 A_{KP1}}{\alpha_2 A_{KP2}} \right) \right] \quad (12)$$

in terms of Kaxiras-Pandey parameters, both of which by virtue of Eqs.(5) and (6). The parameters $\lambda_i R$ and $\alpha_i R^2$ for $i=1,2$ are non-dimensional, and control the shape of the 2-body portion of the Biswas-Hamann and Kaxiras-Pandey potential energy curves respectively in the non-dimensional (U / D) versus (r / R) plane. With only two shape factors in each of the potential functions in the non-dimensional forms, their relationships can be obtained through the imposition of two criteria simultaneously – (i) equal force constant, and (ii) equal mean stretching energy – which were previously imposed in previous works.

Imposition of equal force constant

$$\left(\frac{\partial^2 U_{BH}}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{KP}}{\partial r^2} \right)_{r=R} \quad (13)$$

gives

$$\lambda \lambda_2 = 4\alpha_1 \alpha_2 R^2 \quad (14)$$

while the imposition of equal mean stretching energy

$$\int_R^\infty U_{BH} dr = \int_R^\infty U_{KP} dr \quad (15)$$

leads to

$$\begin{aligned} -\frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2} &= \frac{\alpha_2}{\alpha_1 - \alpha_2} \exp(\alpha_1 R^2) \sqrt{\frac{\pi}{4\alpha_1}} \left[\text{erf}(\infty) - \text{erf}(\sqrt{\alpha_1} R) \right] \\ &\quad - \frac{\alpha_1}{\alpha_1 - \alpha_2} \exp(\alpha_2 R^2) \sqrt{\frac{\pi}{4\alpha_2}} \left[\text{erf}(\infty) - \text{erf}(\sqrt{\alpha_2} R) \right] \end{aligned} \quad (16)$$

where the error function is defined as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n! (2n+1)} \quad (17)$$

or alternatively

$$\text{erf}(x) = \sqrt{1 - \exp\left(-x^2 \frac{(4/\pi) + ax^2}{1 + ax^2}\right)} \quad (18)$$

with

$$a = -\frac{8}{3\pi} \left(\frac{\pi - 3}{\pi - 4} \right) \approx 0.1400. \quad (19)$$

Therefore substituting Eqs.(18) and (19) into Eq.(16) gives rise to

$$\frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2} = \sqrt{\frac{\pi}{4}} \sum_{i,j} \frac{\alpha_j \exp(\alpha_i R^2)}{(\alpha_j - \alpha_i) \sqrt{\alpha_i}} \left[1 - \sqrt{1 - \exp\left(-\alpha_i R^2 \frac{(4/\pi) + 0.14\alpha_i R^2}{1 + 0.14\alpha_i R^2}\right)} \right]. \quad (20)$$

3. Results and Discussion

The validity of the Biswas-Hamann and the Kaxiras-Pandey shape parameter relations shown in Eqs.(14) and (20) can be attested by plotting the Biswas-Hamann potential function, and comparing it with the Kaxiras-Pandey potential energy curve using the parameters of the former. Using the Biswas-Hamann's 2-body interaction parameters

for silicon, $A_{BH1} = 26829.36eV$, $A_{BH2} = 42.59863eV$, $\lambda_1 = 3.946668 \text{ \AA}^{\circ-1}$ and

$\lambda_2 = 1.191187 \text{ \AA}^{\circ-1}$, the corresponding Kaxiras-Pandey parameters can be numerically

solved to give $D = 1.092362eV$, $R = 2.773872 \text{ \AA}^{\circ}$, $\alpha_1 = 1.06250 \text{ \AA}^{\circ-2}$ and

$\alpha_2 = 0.143764 \text{ \AA}^{-2}$. Figure 1 shows the 2-body interaction energy according to the Biswas-Hamann potential (denoted by circles) and the Kaxiras-Pandey potential (smooth curve) converted from the former's parameters.

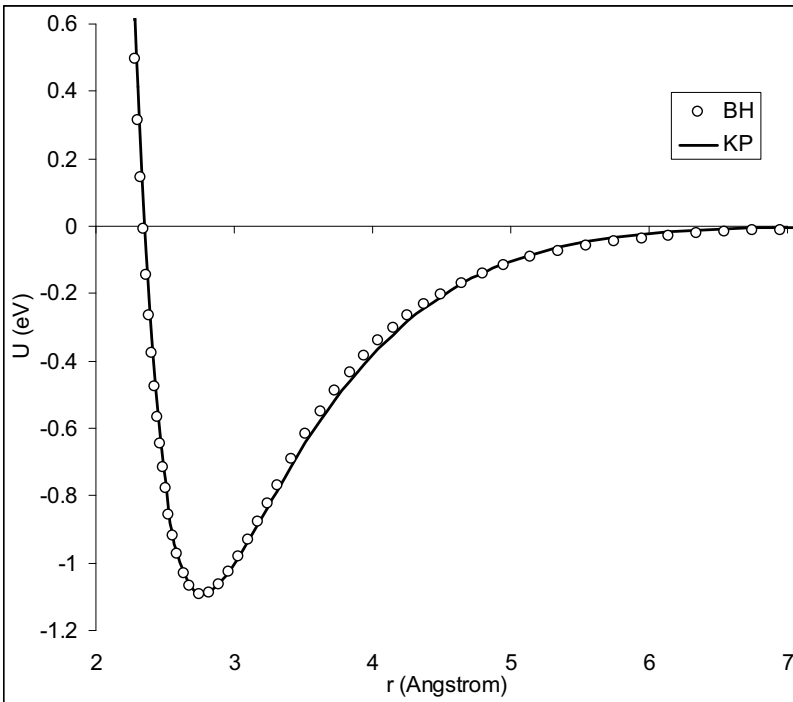


Fig. 1. Obtaining the 2-body energy portion of Kaxiras-Pandey potential energy curve using the 2-body portion of Biswas-Hamann parameters [4].

Even though a close scrutiny reveal a slight discrepancy, it is clear that the use of combined method – equal force constant and equal mean stretching energy – gives very good agreement throughout the entire bond length considered. Although a different technique was previously given for relating the Biswas-Hamann and the Kaxiras-Pandey relations [10], it is felt that the present method possesses better physical justification and hence would render such a method highly applicable for other potential functions. Present results show that the use of this combined technique

for relating the Biswas-Hamann and Kaxiras-Pandey parameters gives better agreement than for relating the Morse and Linnett parameters [18].

4. Conclusions

A method of relating parameters of the Biswas-Hamann and the Kaxiras-Pandey potential energy functions have been developed and tested for its validity. Imposition of equal force constant, which is defined as the curvatures of the potential energy curves at the well-depths' minimum, gives good agreement for bond compression and small bond stretching. Imposition of equal mean bond stretching, defined as the energy integral from equilibrium to dissociation, leads to good agreement for large bond stretching. By combining equal force constant and equal bond-stretching mean energy, impeccably good relationship was observed throughout. The obtain relationship enables parameters of the Biswas-Hamann to be converted into those of Kaxiras-Pandey for application in computational chemistry models that adopt the latter potential, as well as vice versa.

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