Original Research Article

THE COHESIVE ENERGY CALCULATIONS OF SOME BCC (Li, Cr, Fe, Mo) LATTICES USING DENSITY FUNCTIONAL THEORY

ABSTRACT

The cohesive energies of lithium (Li), chromium (Cr), iron (Fe) and molybdenum (Mo) were computed using density functional theory (DFT). DFT based Fritz Haber Institute-ab initio molecular simulation (FHI-aims) computer code has several input parameters in which some of the variables were optimized. The cohesive energies of Li, Cr, Fe and Mo were calculated within local density approximations (LDA) of Perdew Wang of DFT. The results obtained from the calculations of cohesive energies of Li, Cr, Fe and Mo were approximately 1.82eV, 5.33eV, 5.35eV, and 8.02eV respectively. This results obtained are in the neighborhood of experimentally found values of 1.63eV, 4.10eV, 4.28eV and 6.82eV respectively for Li, Cr, Fe and Mo respectively within reasonable percentage errors.

*keywords***:** *bcc; cohesive energy, DFT, ground state, lattice constant, total energy.*

1. INTRODUCTION

Cohesive energy calculations vis-à-vis the first principle total energy calculations using DFT is considered satisfactory in the physics of condensed matter systems, material science and physical chemistry. DFT has a wide application in molecules, bulk materials and surfaces; and remains a reliable tool to analyze as well as predict non-equilibrium and equilibrium properties.

DFT being one of the most popular and quantum-mechanical approaches to many-body systems are applied to computations of ground-state properties of molecules and the band structure of solids in physics. In this computational research work, some selected body-centered cubic (BCC) lattices or crystals were investigated using DFT based FHI-aims code as a tool to calculate the cohesive energies of Li, Cr, Fe and Mo.

This research puts into perspective a single alkaline metal, Li and three transition metals Cr, Fe and Mo. This choice is based on the importance of these materials for modern technology.

Electrochemical batteries as of today are the most (or one of the most) promising energy storage technology in grid integration of renewables, electric vehicles, and electronics devices (Legrain F.C.G, 2016). The batteries have relatively high energy and efficiency and specific example of such batteries is Li-ion battery. Also, lithium has been found effective in assisting the perfection of silicon nano welds in electronic components for electrical batteries and other devices.

Stainless steel and chromium plating (electroplating with chromium) have high commercial use. Iron as well as molybdenum is used in steel alloys, including high strength alloys and superalloys. Indeed these materials have high industrial use and demands. Hence, the needs to further study the cohesive energies of these materials using FHI-aims.

ur interest on structure and binding imply that the cohesive energy E_{coh} of a system is very important. It is useful for studying binding strength in crystal structures and can help to gain information about structural preferences of solids.

42 Cohesive energy is the energy that must be supplied to a solid or crystal to separate its constituents
43 into free atoms at rest and at infinite separation with the same electronic configuration (Kittel 1996,
44 Galperin, 2002). Cohesive energy is one of the parameters used to understand the nature of chemical
45 bonding and several important parameters can be predicted using it. Its magnitude tells us the
46 stability and chemical reactivity of solids. Eventually, it is the quantity which determines the structure,
47 because different possible structures would have different cohesive energies (Verma et al, 2010).
48 Many powerful methods for solving schrodinger's equation have been developed during decades of
49 struggling with the many-body problem. These methods are Nearly-Free-Electron Approximation,
50 Cellular Method, Augumented Plane-Wave method, Scattering Matrix Method, Pseudopotential
51 Method; and other methods. These methods are time-consuming, cumbersome and poses problems
52 to researchers in this field. Hence, DFT as a powerful tool replaces the many-body electronic wave
53 function used in the method mentioned above with the electron density as the basis quantity.
54 In calculating basic properties of solids like cohesive energy, lattice constants, band structures and
55 density of state, we use DFT as the most popular and successful quantum-mechanical approaches to
56 matter (Wienferink, et al,2011).
57 In this research, the cohesive energies of Li, Cr, Fe and Mo were computed based on DFT package
58 FHI-aims code in the range between 1.82eV and 8.02eV which is in reasonable agreement with
59 experimental data in the range between 1.63eV and 6.82eV.
60

61 ## 2.   THEORETICAL FRAMEWORK
62 Density functional theory (DFT) is a quantum mechanical technique used in physics, chemistry and
63 material science to investigate the structural and electronic properties of many body systems. DFT
64 has proved to be highly successful in describing structural and electronic properties in a vast class of
65 materials, ranging from atoms and molecules to simple crystals and complex extended systems
66 (including gases and liquids). DFT has become a common tool in first-principle calculations aimed at
67 molecular and condensed matter systems (Giannozzi, 2005: Parr and Yang, 1989).

68 Traditional methods in electronic structure theory, in particular Hatree-Fock theory and its
69 descendants are based on the complicated many-electron wave function. The main objective of DFT
70 is to replace the many-body electronic wave function with the electronic density as the basis quantity.
71 Whereas many-body wave function is dependent on 3N variables, three special variables for each of
72 the N electrons, the density is only a function of three variables and is a simpler quantity to deal with
73 both conceptually and practically.
74

75 ## 2.1 THE HOHENBERG-KOHN THEOREM
76 It was Hohenberg and Kohn who stated a theorem that tells us that the electron density is very useful.
77 The Hohenberg-Kohn (H-K) theorem asserts that the electron density of any system determines all
78 ground-state properties of the system. In this case the total ground state energy of a many-electron
79 system is a functional of the density.
80

81 Let us consider a system of N interacting (spinless) electrons under an external potential V(r) (usually
82 the coulomb potential of the nuclei). If the system has a non-degenerate ground state, it is obvious
83 that there is only one ground state charge density that corresponds to a given V(r). In 1964,
84 Hohenberg and Kohn demonstrated the opposite, far less obvious result: there is only one external
85 potential V(r) that yields a given ground-state charge density n(r). The demonstration is very simple
86 and involves the disproof of a proposition by showing that it leads to absurdity.
87

88 For many-electron Hamiltonian $H=T+U+V$, with ground state wave function, ψ. T is the kinetic energy,
89 U is the electron-electron interaction. V is the external potential. The charge density $n(r)$ as defined by
90 Hohenberg-Kohn is

91
$$n(r) = N \int \left| \psi \left(r_1, r_2, r_3, \ldots, r_N \right) \right|^2 dr_2 \ldots dr_N$$

92   (2.1)

93

94 Now considering a differential Hamiltonian $H' = T' + U' + V'$. V and V' do not differ simply by a

95 constant: $V - V' \neq$ constant with the ground state wave function ψ' .

96 Assuming that the ground state charge densities are the same: $n[V] = n'[V']$. The following inequality

97 holds:

98
$$E < \left\langle \psi' \left| H \right| \psi' \right\rangle = \left\langle \psi' \left| H' \right| \psi' \right\rangle + \left\langle \psi' \left| H - H' \right| \psi' \right\rangle$$

99   (2.2)

100
$$E < E' + \left\langle \psi' \left| T + U + V - T - U - V' \right| \psi' \right\rangle$$

101   (2.3)

102 That is

103
$$E < E' + \int n(r) \left\{ V - V' \right\} dr$$

104   (2.4)

105 Conversely,

106
$$E' < E - \int n(r) \left\{ V - V' \right\} dr$$

107   (2.5)

108 Adding (4) and (5) gives

109
$$E + E' < E' + E \qquad \text{Contradiction!} \qquad (2.6)$$

110 The inequality is strict because ψ and ψ' are different, being eigen state of different Hamiltonians. By

111 reversing the primed and unprimed quantities, one obtains an absurd result. This demonstrates that

112 no two potentials can have the same density. The first Hohenberg-Kohn (*H-K*) theorem that has a

113 straight forward consequence is that of the ground state energy E is also uniquely determined by the

114 ground-state charge density. In mathematical terms, *E* is a functional *E [n(r)]* of *n(r).* This is why this

115 field is known as density functional theory (Sholl D.S and steckel J.A., 2009). We can write that:

116
$$E[n(r)] = \left(\psi | T + U + V | \psi \right) = \left(\psi | T + U | \psi \right) + \left(\psi | V | \psi \right) = F[n(r)] + \int n(r) V(r) dr$$

117   (2.7)

118 Where *F [n(r)]* is a universal functional of the charged density *n(r)* (and not of *V(r)*) also known as the

119 *H-K* functional (Tuckerman, 2004). For this functional a variation principle holds: the ground state

120 energy is minimized by the ground state charge density; this is the *H-K* second theorem. In this way,

121 DFT exactly reduces the *N*-body problem to the determination of a 3-dimentional function *n(r)* which

122 minimizes a functional *E [n(r)].* Unfortunately, this is of little use as *F [(n)]* is not known.

123 **2.2 THE KOHN-SHAM (KS) EQUATIONS**

124 In 1965, Walter Kohn and Lu Sham proposed an educated guess that later yielded results in which

125 they reformulated the problem in a more familiar form and opened the way to practical application of

126 DFT. The system of interacting electrons is mapped onto a ficticious or auxillary system of non-

127 interacting electrons having the same ground state charge density *n(r).* For a system of non-

128 interacting electrons the ground-state charge density is represented as a sum over one-electron

129 orbitals (the KS orbitals) ψ_i(Martin, 2004):

3

130
$$n(r) = 2\sum_i \left|\psi_i(r)\right|^2$$

131   (2.8)

132   Where i runs from 1 to N/2. If we assume double occupancy of all states, and the Kohn-Sham orbitals
133   are the solution to the Schrödinger equation:

134
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right)\psi_i(r) = \in_i \psi_i(r)$$

135   (2.9)

136   In closed systems, suppose there is an even number of electrons, so that they all can be paired up
137   and the external potential V(r) is independent of spin. Spin-up and spin-down contribute equally to the
138   total density:

139
$$n^{(\uparrow)}(r) = n^{(\downarrow)} = \tfrac{1}{2}n(r)$$

140   (2.10)

141   Therefore, we only need $N_e/2$ Kohn-Sham orbitals, to each of which we assign an occupation number
142   of f=2. These orbitals satisfy the orthogonality condition(Tuckerman, 2004):

143
$$\int \psi_i^* \psi_j(r)dr = \delta_{ij}$$

144   (2.11)

145   Again the density can also be written as:

146
$$n(r) = \sum_{i=1}^{Ne/2} \left|\psi_i(r)\right|^2$$

147   (2.12)

148   And the kinetic energy as

149
$$T_S = -\frac{1}{2}\sum_{i=1}^{Ne/2} \langle \psi_i|(r)|\nabla^2|\psi_i(r)\rangle$$

150   (2.13)
151   The existence of a unique potential V_{KS} in equation (2.9) having $n(r)$ as its ground state charge density
152   is a consequence of the *H-K* theorem, which holds irrespective of the form of electron-electron
153   interaction, *U*. The problem is now to determine $V_{KS}(r)$ for a given $n(r)$. To solve this problem it is
154   convenient to rewrite the energy functionals as:

155
$$E = T[n(r)] + E_H[n(r)] + E_{xc}[n(r)] + \int n(r)V(r)dr \qquad (2.14)$$

156   The first term is the kinetic energy of non-interacting electrons. The second term called the Hatree
157   energy contains the electrostatic interactions between clouds of charges. The third, called the
158   exchange-correlation energy, contains all the remaining terms. The logic behind such procedures is to
159   subtract out easily computable terms which accounts for a large fraction of the total energy. The only
160   term for which no explicit form can be given is E_{xc}.

4

161 Utilizing the *H-K* theorem, we minimize the total energy with respect to the orbitals in order to obtain
162 the orbitals that give rise to the ground state energy. While performing the minimization, we prefer to
163 minimize with respect to $\psi_i^*(r)$ and $\psi_i(r)$. One can prove that both yield the same result.

164 Just like regular differentiation, we can employ chain rule for the functional derivatives. This of course
165 works for all the terms except for kinetic energy. Kinetic energy may be differentiated directly with
166 respect to the orbital. We thus have:

167
$$\frac{\delta E}{\delta \psi_i^*(r)} = \frac{\delta T_S}{\delta \psi_i^*(r)} + \left[\frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_H}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)} \right] \frac{\delta n(r)}{\delta \psi_i^*(r)} = \in_i \psi_i(r)$$

168   (2.15)
169 Finally,

170
$$-\frac{1}{2}\nabla^2 \psi_i(r) + \left[V(r) + \int dr' \frac{n(r')}{|r - r'|} + \{\in_{xc}(r) + n(r)\frac{\delta \in_{xc}[n]}{\delta n(r)}\} \right] \psi_i(r) = \in_i \psi_i \qquad (2.16)$$

171 Where the first, second and third terms in the large brackets gives the KS potential:
172
$$V_{kS} = V(r) + V_H + V_{xc}$$
173   (2.17)

174 Where V_H is introduced as the Hatree potential, and the exchange-correlation potential, V_{xc}.

175 Equation (2.16) is a system of equations, which when solved simultaneously represents the many
176 system in terms of single-particle orbitals.
177 So far, the entire field of DFT rest on two-fundamental mathematical theorems proved by kohn and
178 Hohenberg and the derivation of a set of equations by KS in the mid-1960's (Scholl and steckel,
179 2009).

3. METHODOLOGY

181 In this research, the main production method is DFT to compute the total energy and derived
182 quantities of molecules and solids of condensed matter in its electronic ground state (Blum et al,
183 2009). DFT in the LDA is used here. An all-electron full-potential treatment that is both
184 computationally efficient and accurate is achieved for periodic and cluster geometries on equal
185 footing, including relaxation and ab-initio molecular dynamics (Havu et al, 2009).

186 To calculate the cohesive energies, we first compute the ground state total energies of Li, Cr, Fe and
187 Mo for single free atom and their bulk. The energies are then converted to the cohesive energies

188 using the equation: $E_{coh} = -\dfrac{E_{bulk} - NE_{atom}}{N} = -\left[\dfrac{E_{bulk}}{N} - E_{atom} \right]$
189

                (3.1)
190 All calculations were carried out using FHI-aims code upgrade 6 (released on 17th July, 2011; version
191 071711_6). It works on any Linux based operating system. Computations can only be carried out after
192 building an executable binary file. FHI-aims package is distributed in a source code form and requires:
193 a working Linux based operating system (ubuntu 11.10 in this case), a working FORTRAN 95(or later)
194 compiler. In this case we use x86 type computer and therefore intel's ifort (specifically composerxe
195 2011.6.233) was installed for this work, and also a compiler version of lapack library, and a library
196 providing optimized basic linear algebra subroutines (BLAS). Standard libraries such as intel's mkl or
197 IBM's essl provide both lapack and BLAS support. Intel's composerxe 2011.6.233 comes with mkl.
198 All necessary adjustment were made for building the executable binary file for running the code. FHI-
199 aims require two input files: Control.in:- which contains all run time-specific information and
200 Geometry.in:- which contains information directly related to the atomic structure for a given

201 calculation. The two input files must be placed in the same directory where FHI-aims binary file is
202 invoked at the terminal.
203 The FHI-aims input files are constructed and production run are made to give results in the output
204 files.
205
206 **4. RESULTS AND DISCUSSION**
207 The results from the output files were used to generate tables of values which were in turn used to
208 plot graphs of total energies against number of iterations in order to obtain optimized parameters for
209 BCC (Li, Cr, Fe and Mo) lattices within LDA. The optimized parameters were then used to obtain the
210 cohesive energies of the BCC lattices.
211 Below are results obtained for the calculations of cohesive energies and their discussion:

212
213

214

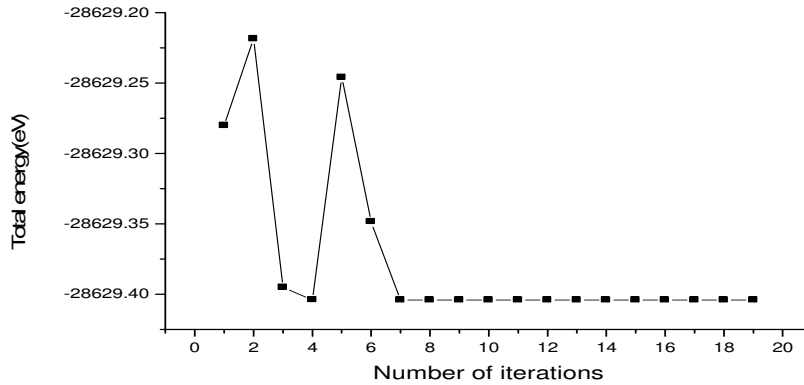215 Fig.1. Binding curve of total energy against no. of iterations for pw-lda Li atom
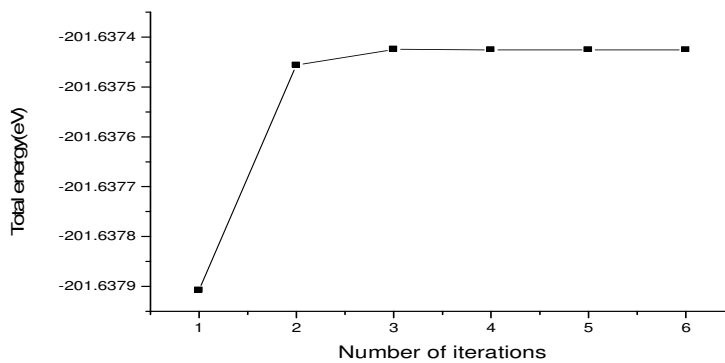
216

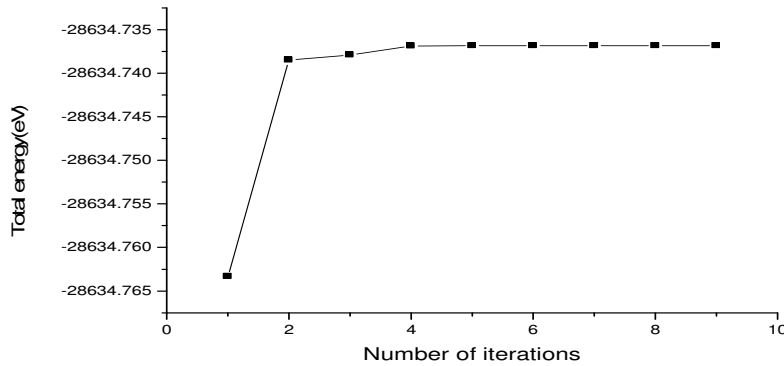217 Fig.2. Binding curve of total energy against no. of iterations for pw-lda Li bulk

218 Fig.1. shows that the total energy decreases while number of iterations increases and converges
219 faster with stability from 3rd iteration to the last iteration because the electrons of lithium atom are
220 pulled closer to the positive charged nucleus(since they are physically closer to the atom and thus
221 less reactive than the other alkali metals. Fig.2. on the other hand shows that the total energy
222 increases with increase in number of iterations, taking more computational time and yielding more
223 stable total energy than Li atom owing to metallic bonding in lithium bulk.

6

224   The cohesive energy obtained for bcc lithium was calculated to be approximately 1.82eV. This result
225   is in good agreement as compared to experimental value of 1.63eV (Dean L., 2016)

226

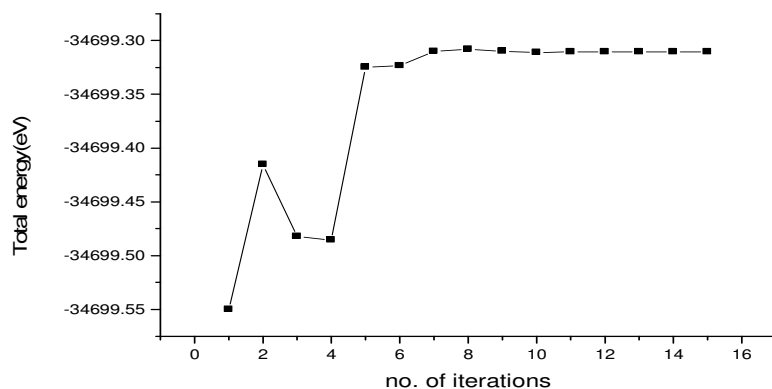227   Fig.3. Binding curve of total energy against no. of iterations for pw-lda Cr atom

228

229   Fig.4. Binding curve of total energy against no. of iterations for pw-lda Cr bulk
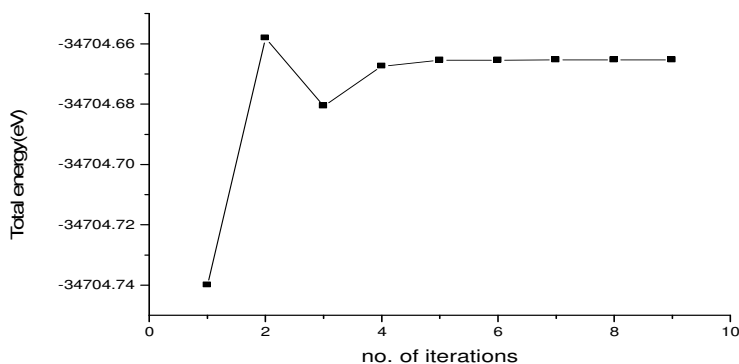
230   From Fig.3, clearly the total energy for single chromium atom is unstable at early iterations due to
231   half-filled and unpaired d-orbital electrons and its eagerness to bond but becomes stable from the 7th
232   iteration. However, the total energy of Cr bulk in Fig.4 becomes stable and converges with fewer
233   numbers of iterations after a sharp rise from 1st iteration to the 2nd iteration.

234   The cohesive energy of bcc chromium is calculated to be approximately 5.33eV which is in
235   reasonable agreement with experimental value of 4.10eV (Jian-Min Z. et al, 2006).

236

237   Fig.5. Binding curve of total energy against no. of iterations for pw-lda Fe atom
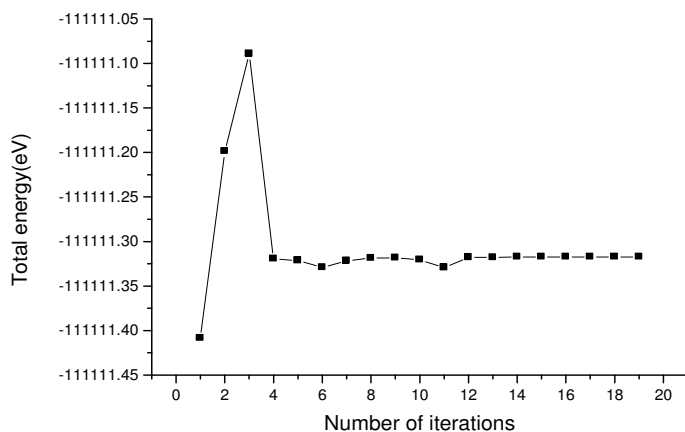

238

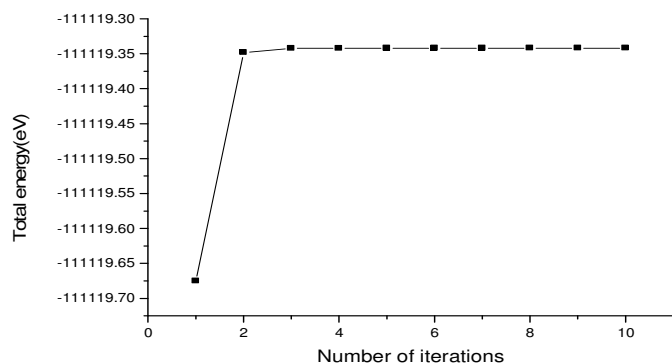239   Fig.6. Binding curve of total energy against no. of iterations for pw-lda Fe bulk

240   Fig.5 shows that the total energy for single iron atom is unstable at early iterations due to unpaired d-
241   orbital electrons and its eagerness to bond but becomes stable from the 7th iteration. In fig.6, the total
242   energy of iron bulk significantly rises from the 1st iteration to the 2nd iteration before a stepwise fall and
243   rise to the 4th iteration to become stable and converged. To attain efficient convergence the linear
244   mixing parameter and broader smearing were chosen carefully since magnetic metals are hard to
245   converge (Wieferink, J. et al. 2011)

246   The cohesive energy was calculated to be approximately 5.35eV which is in reasonable agreement
247   with experimental value of 4.28eV (Jian-Min Z. et al, 2006   ).

8

248

249   Fig.7. Binding curve of total energy against no. of iterations for pw-lda Mo atom

250

251   Fig.8. Binding curve of total energy against no. of iterations for pw-lda Mo bulk

252   Fig.7. shows that the total energy of Mo atom is unstable also due to half-filled d- orbitals and
253   unpaired valence electrons just as chromium discussed above until the 12th iteration when it becomes
254   stable for the rest of the convergence cycles. Fig.8. on the other hand shows that the total energy
255   makes a sharp rise and immediately begins to converge from the 2nd iteration to the last iteration. Mo
256   bulk clearly shows more stability with less number of iterations than Mo atom.

257   The calculated value for cohesive energy bcc molybdenum is approximately 8.02eV which is in
258   reasonable agreement with experimental value of 6.82eV (Jian-Min Z. et al, 2006).

259   5 CONCLUSIONS

260   The contribution of a constituent atom to the total energy E_{tot} might be variationally improved by basis
261   functions sitting on adjacent atoms, thus leading to an overestimating of E_{coh}. Using atomic states,
262   however, the total energy is already converged at the level of the minimal basis, and neighboring
263   basis functions have no effects (R.Gehrke, 2008).

264   The cohesive energies of the bcc lattices were calculated with grids of 12x12x12 for all metals except
265   iron with 16x16x16; a setting which gives a good compromise of computational times and physical
266   accuracy within LDA of the FHI-aims code. The values obtained are in agreement with experimental

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267 values and literature reports within some reasonable percentage error. The cohesive energies
268 calculated for Li, Cr, Fe and Mo vary from experiment by 11.4%, 30.0%, 25.0%, and 17.6%.

269 **REFERENCES**

270 [1] Blum, V., Gehrke R, Hanke F, Havu P, Havu V, Ren X, Reuter K, Scheffler M. "Ab initio molecular
271 simulations with numeric atom-centered orbitals". Computer Physics Communications, 180, (2009),
272 2175-2196.

273 [2] Dean L. "The elements handbook" (Available online at
274 https://www.knowlegdedoor.com/2/elements_handbook/cohesive energy.html. (Accessed on
275 30/08/2016).
276 [3] Galperin, Y. "Introduction to modern solid state physics", (2002). Available @
277 http://wwwgradinetti.org/teaching/chem 121/assests/. (Accessed on 18/08/2016).

278 [4] Gehrke R. "First Principle Basin-Hopping for the Structure Determination of Atomic clusters", 2008.

279 [5] Giannozzi, p. "Density functional theory for electronic structure calculations" struttura della material
280 Vol. I, (2005).

281 [6] Havu V., Blum V., Havu P., and Scheffler M., "Efficient O(N) integration for all-electron electronic
282 structure calculation using numeric basis functions". J. Comp. Phys., accepted (August 13, 2009).

283 [7] Jian-Min Zhang, Yan-Ni Wen, Ke-Wei Xu. "Atomic Simulation of the vacancies in BCC metals
284 MAEAM", Central European journal of physics, CEJP 4(4) 2006 481-493.

285 [8] Kittel, C. "Introduction to solid state physics 7th edition", John Willey, Newyork. (1996).

286 [9] Legrain, F.C.G. "Comparative studies of Li, Na, Mg insertion in elemental group IV materials and
287 oxides: material choices for post-lithium batteries", National university of Singapore, (2016).

288 [10] Martin, R.M. "Electronic structure basic theory and practical methods" (Cambridge university
289 press), (2004).

290 [11] Parr, R. G., Yang,W. "Density functional theory of atoms and molecules" (oxford university press,
291 Newyork), (1989).

292 [12] Sholl, D. S., Steckel, J. A. "Density functional theory: A practical introduction" (A John Willey &
293 sons, inc., publication), (2009).

294 [13] Tuckerman M. "Intoduction to DFT. Maria Currie Tutorial Series: Modelling Biomolecules". Dec. 6-
295 11, 2004.

296 [14] Verma, A.S., Sarkar, B.K. and Jindal V.K. "Cohesive Energy of Zincblende(AIIIBv and AIIBVI)
297 structured solids", pramana journal of physics, India Academy of Science (2010),Vol.74, No.5
298 pp.85855.

299 [15] Wieferink, J., Nemec, I., Blum, V. "Tutorial II periodic systems manuscript for exercise problems"
300 presented at the hands –on tutorial workshop on ab-initio molecular simulation at Friz-Haber Institute
301 der max-planck-Gesellschaft Berlin, July 14, 2011.