Efficacy of surface error corrections to density functional theory calculations of vacancy formation energy in transition metals

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ABSTRACT

We calculate properties like equilibrium lattice parameter, bulk modulus and monovacancy formation energy for nickel (Ni), iron (Fe) and chromium (Cr) using Kohn-Sham density functional theory (DFT). We describe relative performance of local density approximation (LDA) and generalized gradient approximation (GGA) for predicting such physical properties for these metals. We also make a relative study between the exchange correlation functionals, namely, PW91 and PBE, two different flavors of GGA. Our calculations show that DFT is inherently unable to predict the monovacncy formation energy accurately. We calculate the correction for the surface intrinsic error corresponding to an exchange correlation functional using the scheme implemented by Mattson et al. [Phys. Rev. B **73**, 195123 (2006)]. We compare the effectiveness of the correction scheme for the free-electron like Al and 3d-transition metals, namely, Ni, Fe and Cr. The disagreement of the corrected vacancy formation energy with experimental value is found to be less in Al as compared to the transition metals. The reasons for the ineffectiveness of this correction scheme in 3d-transition metals are discussed.

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I. INTRODUCTION

Using fundamental laws of quantum mechanics to predict material behavior on atomic scale has become very popular during last few decades.[1] *Ab initio* calculations are playing a crucial role in understanding physics, chemistry and biology. The Kohn-Sham (KS) density functional theory[2] (DFT) based electronic structure calculation is a widely accepted and most successful method in this field. According to Kohn,[3] DFT focuses on quantities in real, three dimensional coordinate spaces, mainly on ground state electron density.[3] The single particle KS equations, in principle, account for all ground state many body effects when used with exact exchange correlation (XC) functionals.[3] Therefore, it is clear that practical usefulness of DFT for describing ground state properties depends entirely on whether approximations for this XC functional could be found which are sufficiently simple and accurate. The simplest approximation of XC functional is the local density approximation (LDA).[2,4] In this approximation, XC functional depends on the exchange correlation energy per particle of a uniform electron gas of a given density. This prescription is exact for a uniform electron gas and *a priori* expected to be fairly accurate for systems having a slow variation of electronic density on the scales of local Fermi wavelength and Thomas Fermi wavelength.[3] LDA can fail in systems where electron-electron interaction effects are dominant. An important improvement over LDA is the generalized gradient approximation (GGA) of electron density where the XC functional depends on electron density and its spatial variation.[5,6,7] But all such treatments of XC functional and its consequent improvements may be inappropriate in systems for which assumption of uniform or slowly varying electron density is

inapplicable.[8] According to Kohn and Mattson,[8] the KS single particle wave function makes a transition from oscillatory to a decaying type where the electron charge density makes a sharp jump. Therefore, the uniform density based assumption of DFT, breaks down in describing such cases. One such situation arises due to the presence of a vacancy in a material, since it introduces a steep variation of electronic density near the vacant site.[9,10] Such electronic density gradient resembles the variation near a surface region of a material.[9] This gives rise to a qualitative difference between the perfect bulk and a system with a vacancy. The DFT based total energy calculation of such a system leads to inaccurate estimation of vacancy formation energy.[9]

 According to Mattson and Kohn,[10] there are two complementary ways to improve the accuracy of a DFT calculation of vacancy formation energy:

(1) First, one can continue to develop more accurate local, quasi-local or universal approximations such as LDA, GGA and weighted density approximation all of which presume enough local resemblance with a uniform electron gas. Armiento et al.[11] designed a DFT XC functional, AM05 that can treat systems with electronic surfaces better than previously available XC functionals.[11] Very recently Perdew et al.[12] proposed a revised version of PBE, known as PBEsol, for treating solids along with their surfaces.[12] Later this PBEsol functional was tested by Ropo et al.[13] for bulk properties of 3d metals where the measure of inaccuracy for both PBE and PBEsol were seen to be comparable.[13] They concluded that the two newly developed functionals AM05 and PBEsol are superior in estimating metallic bulk and surface properties to former gradient

level approximation.[13] Through these improvements of XC functionals, the accuracy in the estimation of vacancy formation energy by DFT can be improved.

 (2) The second method involves dividing the material into two regions.[10] In one part of the system, away from the vacancy, the usual method of DFT holds well, whereas in the other part of the system in the immediate neighborhood of the vacant site, use of DFT is not accurate. This region is treated differently with other methods. This region, at the interface between the bulk and the vacant site, can be treated by an analytic formulation or by Monte-Carlo methods. Finally, these two results are integrated such that both the descriptions are well matched at the boundary.[10]

In the present work, we adopt the ideas of the second method but make a useful variation. To start with, we treat the whole system with DFT. Since, DFT is known to be inaccurate in describing the surfaces of a vacancy, we need to introduce a correction in the energetics of the region around the vacant site. A general outline for this scheme is as follows:[9,10,14,15] First, the surface is approximated to represent that of a simplified reference system devoid of the detailed spatial structure. For this reference system, a surface self-energy correction (energy/unit surface area) is determined as a function of electron density related parameters of this system. Secondly, the density of the actual system is invoked to get the reference system parameters. This correction scheme was first developed by Mattson and Kohn, where the reference system has an exponential variation of the effective KS single particle potential in the region near the surface.[10] This model is based on two parameters, one depends on the bulk density and the other describes the density profile at the surface. However, for this model while the surface

exchange energy data are available, the surface correlation energy data are not available. Therefore, we would not be able to obtain the required accuracy in calculating the correction for the surface self-energies.[9] Since, exact data of both surface exchange and surface correlation energy are available for a jellium surface;[9] we use a correction scheme based on jellium surface model.[14] This model was first implemented for the evaluation of surface intrinsic error by Mattson et al.[9] Here, the bulk density is the only adjustable parameter.[9,15] The mapping from real system to one parameter reference system is done by using the mean bulk density of the real system.[9,15] Mattson applied this correction scheme for Pt, Pd and Mo, and showed that the corrected values of vacancy formation energy were in good agreement with experimental data available.[9] But in this scheme, it is assumed that PW91[5,6] and PBE[7] have the same surface intrinsic error and they applied PBE corrections to PW91 results.[14] Later, Mattson et al.[14] showed that PBE's performance at surface is better than PW91, but still not as good as LDA's performance.[14] Therefore, they derived a new scheme for the surface intrinsic error correction specific for PW91, and also derived new simplified surface corrections for PBE and LDA.[14] An important assumption in their approach is to use the known error of a functional in one system as a correction in a similar system with unknown error.[14] They calculated XC surface energies (σ_{XC}) for jellium surface, for each XC functional. They also calculated the most accurate XC jellium surface energies (σ_{XC}^{RPA+}) for the same XC functional, using the "improved random phase approximation" (RPA+).[16] The difference of these two surface energy terms, $\Delta\sigma_{XC} = \sigma_{XC} - \sigma_{XC}^{RPA+}$, is used as the correction for surface energies for that particular XC functional in general.[14] In compact parameterized form, the surface intrinsic error is given by:[14]

$$\Delta\sigma_{XC}(\tilde{r}_s) = A\tilde{r}_s^{-5/2} + B\tilde{r}_s^{-3/2} \quad . \tag{1}$$

Here, $\tilde{r}_s = \dfrac{r_s}{a_{Bohr}}$, a_{Bohr} = Bohr radius and r_s = Wigner Seitz radius defined as,

$$r_s = a_{lat}\left(\frac{3}{4\pi M N_{elect}}\right)^{\frac{1}{3}} = \left(\frac{3}{4\pi\overline{n}}\right)^{1/3} \quad ; \tag{2}$$

where, a_{lat}, M and N_{elect} represent equilibrium lattice parameter, number of atoms per unit cell and number of outermost electrons per atom respectively and $\overline{n}$ is the electron density in the material. For LDA, the values of A and B are estimated to be 0.028 eV/Å^2 and -0.0035 eV/Å^2 respectively.[14] For PW91, the values of A and B are estimated to be 0.0984 eV/Å^2 and -0.0144 eV/Å^2 respectively.[14] For PBE, the values of A and B are estimated to be 0.0745 eV/Å^2 and -0.0109 eV/Å^2 respectively.[14] Mattson et al. implemented this intrinsic surface correction scheme to vacancy formation energy for Pt, Pd and Mo and showed that the corrected values of vacancy formation energies are in good agreement with experiment.[14] But the success of such model based correction scheme, in a more general context, needs to be examined, especially for studying vacancy in transition metals where a jellium picture may not be a good description.

We have chosen 3d-transition metals in order to examine the validity of such an approach. Descriptions of many electronic properties of 3d-transition metals, by DFT using LDA and GGA, are known to be erroneous owing to the delocalized mixed character of the 3d-states.[17] Thus, it is interesting to examine the use of the results of a jellium model to correct for the surface effects in the vacancy formation energy. Inspired by this, we perform KS DFT calculations of vacancy formation energy for nickel (Ni),

iron (Fe) and chromium (Cr) for which 3d-orbitals play an important role to decide their physical properties.

II. CALCULATION DETAILS

We perform the DFT calculations using VASP[18,19,20] (Vienna Ab initio Simulation Package) code, using plane-wave basis set. In the present calculation we use projector augmented wave[21] (PAW) as well as ultrasoft[22] (US) formalism based pseudopotentials (PPs). For PAW PPs we use PBE,[7] PW91[5,6] and LDA[4] XC functionals whereas for US PPs only PW91 and LDA XC functionals are used. All the PPs are taken from the VASP PP library. We take great care in convergence of all results with respect to system size, basis sets and k-points as discussed in Appendix. All calculations done here are based on supercell based approach. We perform the calculations with various supercell sizes to check the dependence of results on system sizes. We find that $4 \times 4 \times 4$, $3 \times 3 \times 3$ and $3 \times 3 \times 3$ supercells for the Ni, Fe and Cr respectively provide good convergence of total energy per atom to less than 10^{-3} eV. Unconstrained minimizations have been carried out for all calculations. We perform spin polarized calculations for all three systems. For Ni and Fe we use ferromagnetic model whereas for Cr we use a simple antiferromagnetic model where the two sublattices have alternating spin configurations. The common settings of DFT calculations for Ni, Fe and Cr are summarized in Appendix.

III. RESULTS AND DISCUSSIONS

Here we discuss the results of the computation described above. In section A, we discuss the equilibrium lattice parameters and bulk modulus for Ni, Fe and Cr. In section B, we

present the results of the calculation of vacancy formation energies for these metals. In section C, we describe a comparative study of the results obtained from calculations done by PW91 and PBE XC functionals.

A. Equilibrium lattice parameter and bulk modulus

At first we calculate bulk properties like equilibrium lattice parameter and bulk modulus of Ni, Fe and Cr and compare the results with available experimental data. The values of equilibrium lattice parameter, a_{lat} (in Å) and bulk modulus (B_0) (in GPa) corresponding to different PPs are tabulated in Table I. In fact, a_{lat} and B_0 (along with cohesive and sublimation energy) are taken as essential inputs into formulation of empirical effective interatomic potentials employed for computation of defect properties by lattice static Green's function method and lattice static simulation.[24,25,26,27,28] However, we calculate these bulk properties from basic electronic structure computation and compare the values with experimental data with a view to validate the parameterized XC functionals; these functionals are, in turn, employed in the estimation of vacancy formation energy. To obtain B_0, we calculate the total energy for different lattice parameters of the fully relaxed cells and find the lattice parameter corresponding to minimum energy by fitting with Murnaghan's equation of state.[29]

From Table 1, we notice that among PAW PPs, PBE and PW91 XC functionals make accurate estimates of equilibrium lattice parameter of Ni, whereas LDA underestimates this value by ~3% when compared with experimental value. In case of Ni, the performances of PW91 and LDA XC functionals for both US and PAW PP formalisms to calculate a_{lat} are comparable. Both PBE and PW91 (PAW and US) underestimate a_{lat} for

Fe and Cr by ~1% and ~2% respectively, LDA (PAW and US) underestimates the same by ~4%. Similarly, for bulk modulus, in case of Ni, LDA (PAW and US) grossly overestimates the experimental value of B_0 as compared with PW91 and PBE values for both PAW and US PP based approach. In case of Fe, PW91 and PBE when used under PAW PP formalism overestimates B_0 by ~20% and underestimates it by the same amount while using under US PP formalism, whereas, for LDA, both PAW and US, B_0 lies with in ~40-50% of experimental data. Though for Cr, PAW PBE and US PW91 give better agreement with experiment, PAW PW91 and LDA values differ significantly from the experimental values. Although undesirable, encountering such large differences could have been arisen because of the effect of ignoring the atomic cores in our formalism and the associated error might get enhanced as it gets propagated into physically differential properties like the elastic modulus. In summary, we find that (1) GGA gives better agreement with experiments in computing bulk properties, at least for the calculations of equilibrium lattice parameter and bulk modulus; (2) Within PAW PP formalism, both PBE and PW91 produce similar results except for Cr for which B_0 values differ significantly; (3) For PW91 XC functional, PAW and US PP based results of a_{lat} and B_0 are markedly different for Fe and Cr, whereas for Ni, the results are comparable; (4) For LDA XC functional, both PAW and US based calculations produce similar results. These observations suggest that the process of selecting an XC functional for a simulation should be given careful attention. It is known that a universal XC functional would not work for a material in all situations.[30] This is, possibly, at the root of the observed disagreement of our results obtained from different models. In Fig. 1, we have plotted the density of states (DOS) vs. energy, for a fixed lattice constant of Ni for both PAW PBE

and PAW LDA. This plot shows that the valence energy spectra of Ni for PAW PBE and PAW LDA are identical in nature, in agreement with Ruban et al.[17], for 3d metals. It may be noted that in all these approaches the atom cores are ignored; and the consequences of this are expected to be different in GGA and LDA models. Hence, the inadequacy of considering only the valence electrons, whose contributions are essentially identical, might account for the eventual disagreements in the final results.

B. Vacancy formation energy

The formation energy is calculated using the following formula:[9]

$$E_f^v = E(N-1,1) - \frac{N-1}{N} E(N,0) \tag{3}$$

Here, E(N,0) represents total energy of the perfect system with N atoms of the supercell and E(N-1,1) is the energy of the system when one of the atoms is replaced by a vacancy. Calculated vacancy formation energies and the corresponding existing experimental and computed data available in literature are tabulated in Table II for Ni, Fe and Cr. Comparison with literature validates the accuracy of our method of calculation. Some common observations from this table are following:

Both LDA and GGA underestimate vacancy formation energy for Ni. Both PBE and PW91 versions of GGA underestimate vacancy formation energy by ~20% as compared to experimental value for Ni whereas LDA underestimates this within ~6%. In case of Fe, for all calculated values better agreement is seen with experimentally available data. LDA overestimates this by a small amount. Vacancy formation energy for Cr is overestimated considerably by all functionals. PAW PBE makes an overestimation by ~

40% which is quite large. Other XC functionals also overestimate these values by ~20%. These observations indicate that even the calculations of monovacancy formation energy for these metals, using first principle techniques, are not accurate enough. In our calculations lattice relaxations are included. According to Mattson,[9] DFT underestimates the vacancy formation energy when the effect of structural relaxation is incorporated, however, our present work points contrary to this statement as both positive and negative errors in calculated values of E_f^v are encountered in different systems. The defect structures, like vacancies, are associated with surface like attribute. It is known that, LDA treats this aspect of the surface better than GGA.[14] Further, as the errors in exchange and correlation effects cancel more effectively in LDA formulation as compared to GGA,[14] the vacancy formation energies obtained using LDA with different PPs exhibit better consistency than GGA. Our results tabulated in Table II support this view. As mentioned earlier, we have carried out spin polarized calculations for all of the three metals. Our study supports the fact that both Ni and Fe have ferromagnetic ground state. Magnetic moment values per unit cell for Ni, Fe and Cr are found to be 2.52, 4.4 and 0 Bohr Magneton, respectively, which are in good agreement with experimentally available data.[31] However, for Cr, we have used a simple antiferromagnetic configuration though the magnetic ground state of Cr is controversial.[32] Even after spin relaxation, the eventual magnetic moment was seen to be zero, supporting our model of the ground state. However, the source of large deviations in the vacancy formation energy from experimental data in Cr is not clear.

C. PW91 vs. PBE

We have compared the values of equilibrium lattice parameters, bulk modulii and monovacancy formation energies of Ni, Fe and Cr for PW91 and PBE XC functionals under PAW based PP formalism. Results for the equilibrium lattice parameter, a_{lat} and bulk modulus, B_0, as shown in Table I, are similar. Because most of the XC functionals and their code implementations are typically tested to match a_{lat} and B_0, the negligible difference of values between PBE and PW91 is understandable.[14] We now turn to the monovacancy formation energy E_f^v. For Ni, Fe and Cr, the differences are 0.05 eV, 0 eV and 0.53 eV respectively. The way PW91 was implemented in VASP code is different from standard implementation, especially for spin-polarized calculations.[14] This may be regarded as the reason for getting small difference for PW91 and PBE for Ni and Fe. Mattson et al.[14] also mentioned about similar observation for monovacancy formation energy of Pt with VASP code. However, the difference of E_f^v values in Cr for PW91 and PBE is rather large. The origin of such pronounced difference for Cr can not be attributed to the basis set insufficiency. While the exact reason is not clear, we conjecture that it may be due to nonequivalence of the treatment of surface regions[14] for the two GGA functionals, namely, PW91 and PBE.

IV. Surface self-energy corrections

As the discrepancy in E_f^v has important consequences, there has been efforts to narrow down the differences by incorporating surface self-energy corrections in several metals.[9,10,14,15] We have attempted this for Ni, Fe and Cr and the results are discussed in the following section.

The surface self-energy corrections have been calculated using the method suggested by Mattson et al.[14] As a check of implementation into VASP calculation, we have repeated their calculation for Al and established the matching before we proceed to computation for Ni, Fe and Cr. In addition, we have developed another way of estimating the exposed surface area due to a vacancy. For comparison, we include, in the following, the results for Al also.

In Figs. 2a, 2b, 2c and 2d, we plot the valence electron density in the (001) plane for the perfect systems of Al, Ni, Fe and Cr. These plots show that for Ni, Fe and Cr, valence charges density is maximum at lattice sites and depleted considerably away from the atoms. However, in Al, the valence electron density is minimum at atomic sites and is seen to spread over the interstitial spaces. We have also plotted, in Figs. 2e, 2f, 2g and 2h, the valence electron density around the vacant lattice site in the (001) plane for Al, Ni, Fe and Cr respectively. The normalized charged density (charge density/maximum charge density) vs. r/d along the close packed direction of Al, Ni, Fe and Cr for both perfect crystal and the crystal having a vacancy are shown in Fig.3. From these plots, it is clear that, the vacancy has been created in Al at a site where valence charge density is already low; but for Ni, Fe and Cr, vacancies have been created at high charge density region. Further, the comparison of figures 3a and 3b shows an increase of valence charge density by ~10% at vacant lattice site in Al, whereas, for Ni, Fe and Cr, the valence charge density at vacant site decreases by ~100%. The plot, as shown in Fig. 2e, also suggests that whenever a vacancy is introduced in Al, electrons surrounding the vacant site move

towards it, thereby, resulting in a slow variation of electronic density at the interface. But for Ni, Fe and Cr, as observed from Figs.2f, 2g and 2h respectively, valence electrons remain concentrated near atomic cores and therefore, no significant change in electronic density ensues in and around the vacant sites. Therefore, unlike Al, creation of vacancies in Ni, Fe and Cr result in abrupt change of valence electron density around the vacant sites. This becomes evident also from the plots shown in Fig.3b. The feature of the change in electronic density is similar to the variation in the charge density near the surface region of a system. In such a region, the basic assumptions of DFT, namely, the uniform or slowly varying electronic density does not hold good.[8] Therefore, the error in DFT based calculation of vacancy formation energy of free-electron like Al would be less than in the case of transition metals like Ni, Fe and Cr. From our present calculations, we notice that DFT makes ~ -9% error in the estimate of E_f^v for Al, whereas for Ni, Fe and Cr, the errors are in the range of ~ -20%, ~ +8% and ~ +40-50% respectively. There is no clear understanding of the direction and actual magnitude of the deviations from the experimental values. In our present study, we have evaluated the surface self-energy contribution to the vacancy formation energy. This involves two main considerations stated as follows:[14]

First, we need to use Equation 1 for evaluating the surface self-energy correction per unit area. This is done by using the electron density $\bar{n}$ obtained as MN_{elect}/a_{lat}^3.[9,15,33] Secondly, we need to estimate the exposed surface area because of the creation of vacancies. This is performed in two ways. In one, we have followed Mattson and scaled the equivalent sphere radius from the value for Al as given by Carling et al. But for the bcc Fe and Cr, this is further scaled by the ratio, $\sqrt{3/2}$, of the nearest neighbor distances

in bcc and fcc lattices.[9] We have also computed the exposed surface area by using the vacancy formation volume given by:[33]

$$V_f = V(N-1,1) - \frac{N-1}{N}V(N,0) \ . \tag{4}$$

Here, V(N,0) and V(N-1,1) represent the volume of a N atom system and the system where one atom is replaced by a vacancy respectively. We obtain the values of V_f from our first principle calculations. Whenever a vacancy is created in a material, other atoms in the system relax. The degree of relaxation is more for neighboring atoms of the vacant site and it decreases in the farther neighboring shells. The exposed surface can be regarded as the surface enclosing the volume around the vacant lattice site after full relaxations. This volume is regarded as the vacancy formation volume V_f, which is calculated according to the equation (4). Now, this volume is approximated to be an equivalent sphere. In the second way of calculating exposed surface area, we have used the radius of this sphere and obtain the exposed surface area as $\left(36\pi V_f^2\right)^{1/3}$. Thus knowing the bulk electron density and using the correction scheme discussed earlier, we calculate the intrinsic surface error per unit area and finally estimate the total correction by multiplying the error/area with the net exposed area. In order to test the method, we have carried out a calculation using PAW potential with PBE as XC functional for Al for which experimental as well as computed data are already available in literature.[14] We obtain the values for equilibrium lattice constant and bulk modulus by fitting the free energy vs. volume data to Murnaghan equation of state. In Table III we compare our results with the experimental values as well as calculated values by Mattson et al.,[14] who also used the PAW PBE PP for their calculation. In our calculation for Al, we estimate

the exposed surface area from first principle technique as mentioned above. The comparison is really satisfactory.

In table IV, we present the calculated values of the exposed surface area for a monovacancy in Ni, Fe and Cr, using different XC functionals. We also tabulate the bulk electron density values for these metals, the surface self-energy correction per unit area and the total correction corresponding to each XC functional. Table V shows the detailed comparison between experimental values of the vacancy formation energy, their calculated values with and without correction for the surface intrinsic error. In tables IV and V, we have labeled the columns containing data using exposed surface area calculated by Mattson's technique as "MATT" and the columns of data using exposed surface area by first principle technique as "FP".

In Table IV, we notice that the intrinsic surface error per unit area calculated from equation (1) is minimum for LDA based XC functionals and maximum for PW91 XC functionals in all kind of PPs. The correction for PBE and PW91 are also different. Calculated values of exposed surface area differ largely between "MATT" and "FP" using PW91. LDA, however, offers good match between "MATT" and "FP" values. Earlier in this paper we expressed the possibility and expectation of improving the estimate of the vacancy formation energy by incorporating the surface energy corrections in general for all metals. This implies a positive correction is needed for Ni, negligible correction for Fe and a negative correction for Cr. The energy correction can be negative when obtained through Equation (1), when $\widetilde{r}_s > 8$ for LDA and $\widetilde{r}_s > 6.8$ for PBE and

PW91. This is a result of the assertion of Ref. [14] where the values of A and B are given for general use. Since, the calculated $\tilde{r}_s$ values, as shown in Table IV, are far less than these numbers, the corrections are always seen to be positive. In fact, for metals such large values of $\tilde{r}_s$ can not be realized implying the surface self-energy corrections can never be negative. Table V shows that after implementing the correction, the values (both "MATT" and "FP") for vacancy formation energies become worse when compared with the experimental values. Mattson et al.[14] have pointed out that even for Al, where the jellium model should work better; the surface self-energy correction further widens the gap between the computed and experimental vacancy formation energy rather than bridging it.[14] Our comparative study of Al, Ni, Fe and Cr clearly demonstrates that the disagreement of computed values from experimental values is less in Al as compared to the cases of the transition metals.

In Figs.2 and 3, we have already observed that, Al is more like a free-electron system, whereas, in Ni, Fe and Cr, valence electrons are almost localized at the atomic sites. Therefore, a jellium should describe the electron distribution of Al well. In the jellium model, the metal is regarded to consist of interacting electrons in which a uniform positive charge background exists to maintain charge neutrality.[34] At zero temperature, the properties are dependent only on the electronic charge density.[34] Therefore, this gives a fair approximation for free electron systems like the s-band[34] and sp bonded metals.[35] Though jellium model can explain free electron and nearly free electron systems fairly well, it suffers from some drawbacks. This model leads to error in the wavefunctions near the atomic core.[34] The model can not describe the d-bands of Ni, Fe and Cr properly,

since the d electrons are localized around atoms and their wavefunctions substantially differ from that of the free electrons.[34] Jellium based models fail to account for the s-d coupling encountered in transition metals.[34] The band structures of transition metals reveal the existence of band edges a few electron volts below the Fermi level.[34] The wavefunctions near such band edges are important in the considerations of the surface properties.[34] Thus, the jellium based models can not adequately account for the surface contributions to the vacancy formation energy in 3d-transition metals.

V. CONCLUSIONS

The detailed DFT study of bulk properties like equilibrium lattice parameter and bulk modulus for the 3d-transition metals like Ni, Fe and Cr, using various XC functionals under PAW and US PP based formalisms, has been carried out. It shows that GGA gives better estimate of these equilibrium properties than LDA for these metals. A general combination of XC functional and PP formalism can not be identified to work well for all situations. However, LDA is seen to be more consistent than GGA in predicting monovacancy formation energy for these metals. Our result demonstrates that both LDA and GGA PP based DFT calculations make inaccurate estimate for vacancy formation energy. The mismatch between reported experimental value and the computed value for Cr is quite large. Therefore, we conclude that even the so-called simple problem of calculating vacancy formation energy is not straightforward. Attempts have been made to resolve this issue using a jellium based model developed by Mattson et al.[14] who implied its universal applicability contrary to our results. In fact, a negative surface energy correction, often needed as in the case of Cr, in high electron density systems like metals,

is impossible to obtain using this formalism. Thus, in many cases the surface energy correction increases the disagreement with experiments in stead of reducing it. Although this effect is small in Al, it is considerably large in the 3d transition metals, namely, Ni, Fe and Cr, studied here. We have analyzed the reason for its marked failure in accounting for the 3d transition metals. In this work, we also report evidence for the non-equivalence of PBE and PW91 though we do not establish it unambiguously and quantitatively.

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APPENDIX

Common settings for all Ni calculations: plane wave cutoffs are ~337.0 eV for PAW PBE, PAW PW91, PAW LDA and ~302.0 eV for US PW91 and US LDA whereas the recommended cutoff energies (ENMAX) are 269.533 eV, 269.561 eV, 269.618 eV, 241.622 eV and 241.683 eV for PAW PBE, PAW PW91, PAW LDA, US PW91 and US LDA respectively. Augmentation used ~545 eV for PAW PBE, PAW PW91, PAW LDA, and ~405 eV for US PW91 and US LDA. In all calculations for Ni the numbers of k-points used are 5 ×5 ×5 in the Monkhorst-Pack scheme.[23] This gives the convergence of ~10^{-5} eV for the total energy per atom.

Common settings for all Fe calculations : plane wave cutoffs are 335.0 eV for PAW PBE, PAW PW91, PAW LDA and ~297.0 eV for US PW91 and US LDA whereas the

recommended cutoff energies (ENMAX) are 267.883 ev, 267.907 ev, 267.969 ev, 237.510 eV and 237.587 eV for PAW PBE, PAW PW91, PAW LDA, US PW91 and US LDA respectively. Augmentation used ~511.4 eV for PAW PBE, PAW PW91, PAW LDA and ~400 eV for US PW91 and US LDA. In all calculations for Fe the numbers of k-points used are 6 ×6 ×6 in the Monkhorst-Pack scheme.[23] This gives the convergence of ~10^{-5} eV for the total energy per atom.

Common settings for all Cr calculations : plane wave cutoff s are ~350.0 eV for PAW PBE, PAW PW91, PAW LDA, US PW91 and US LDA whereas the recommended cutoff energies (ENMAX) are ~227 eV. Augmentation used ~402 eV for PAW PBE, PAW PW91, PAW LDA and ~384 eV for US PW91 and US LDA. In all calculations for Cr the numbers of k-points used are 6 × 6 × 6 in the Monkhorst-Pack scheme.[23] This gives the convergence of ~10^{-5} eV for the total energy per atom.

For all calculations mentioned above the energy tolerance for electronic iterations are 10^{-6} eV and Fermi smearing value is 0.2 eV. All calculations are performed with "PRECISION = HIGH" in the INCAR files.

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Figure Captions:

FIG. 1. (Color online) Density of states (DOS) plot of Ni calculated with experimental lattice constant (2.867 Å) for spin up configuration. Solid line and dashed line stand for PAW LDA and PAW PBE PPs espectively.

FIG. 2. (Color online) Contour plots of electronic charge density in (a) the (001) plane of Al, (b) (001) plane of Ni, (c) (001) plane of Fe and (d) (001) plane of Cr for perfect lattice structures. Contour plots of electronic charge density in (e) the (001) plane of Al around the vacancy, (f) (001) plane of Fe around the vacancy, (g) (001) plane of Fe around the vacancy and (h) (001) plane of Cr around the vacancy. Charge density is expressed in electrons/$Å^3$.

FIG. 3. (Color online) One dimensional plots of normalized charge density vs. r/d (a) for perfect lattice and (b) for the lattice having a vacancy. In both cases normalized charge density is defined as a ratio of charge density to maximum charge density for the same metal. Here r is distance and d is nearest neighbor distance along closed packed direction.

Table Captions :

TABLE I. The computed DFT values of equilibrium lattice parameters and bulk moduli of Ni, Fe and Cr. The numbers are calculated using various flavors of pseudopotentials : PAW PBE, PAW PW91, PAW LDA, US PW91 and US LDA. The computed values are compared with experimental values.

TABLE II: Vacancy formation energies for Ni, Fe and Cr are calculated using PAW (PBE, PW91, LDA) and US (PW91, LDA) pseudopotentials by DFT. Calculated values are compared with experimental data as well as other computed data.

TABLE III: The computed DFT values of equilibrium lattice parameter, bulk modulus, vacancy formation energy, corrected vacancy formation energy are calculated using PAW PBE pseudopotential. The numbers are compared with experimental values[33] as well as data as calculated by Mattson *et al.*[14]

TABLE IV: The computed values of exposed surface area as well as corresponding surface corrections are calculated. Exposed surface area are calculated using Mattson's technique (labeled as "MATT") as well as *ab initio* method (labeled as "FP"). Wigner-Seitz radius (r_s) are calculated using Equation 2.

TABLE V: Corrected values of vacancy formation energies are compared with experimental values. Corrected values using exposed surface area obtained from Mattson's procedure and *ab initio* technique are labeled as "MATT" and "FP" in corresponding columns respectively.

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TABLE I. The computed DFT values of equilibrium lattice parameters and bulk moduli of Ni, Fe and Cr. The numbers are calculated using various flavors of pseudopotentials : PAW PBE, PAW PW91, PAW LDA, US PW91 and US LDA. The computed values are compared with experimental values.

Metals	Experimental value		Calculated values using PP based KS DFT									
			PAW PBE		PAW PW91		PAW LDA		US PW91		US LDA	
	a_{lat} (Å)	B_o (GPa)	a_{lat} (Å)	B_o (GPa)	a_{lat} (Å)	B_o (GPa)	a_{lat} (Å)	B_o (GPa)	a_{lat} (Å)	B_o (GPa)	a_{lat} (Å)	B_o (GPa)
Ni	3.524[a]	180[a]	3.523	193.635	3.52	196.743	3.426	252.468	3.533	196.186	3.432	235.353
Fe	2.866[a]	170[a]	2.834	204.0	2.827	199.095	2.747	252.234	2.860	135.828	2.762	237.457
Cr	2.910[a]	160[a]	2.855	177.235	2.841	212.345	2.779	305.626	2.893	134.888	2.787	270.125

[a]Reference 36

TABLE II: Vacancy formation energies for Ni, Fe and Cr are calculated using PAW (PBE, PW91, LDA) and US (PW91, LDA) pseudopotentials by DFT. Calculated values are compared with experimental data as well as other computed data.

Metal	Experimental Value (eV)	Present Work					Computed data by others	
		PAW pseudopotential			US pseudopotential			
		PBE	PW91	LDA	PW91	LDA		
Ni	1.78[a] 1.8[b] 1.79[d]	1.45	1.4	1.68	1.41	1.7	1.77[e] 1.62[f] 1.37[f]	FP LMTO DFT (LDA) DFT (GGA)
Fe	2±0.2[c]	2.16	2.16	2.26	1.98	2.33	1.95[c] 1.93-2.07[c] 2.07[c] 2.12[g] 1.93[g]	VASP PW PWSCF PW SIESTA VASP PAW GGA VASP USPP GGA
Cr	2.27[d] 2.0[b]	3.18	2.65	2.86	2.76	2.82	2.86[e] 2.81[g] 2.81[g]	FP LMTO VASP PAW with AFM configuration VASP USPP with AFM configuration

[a]Reference 37
[b]Reference 38
[c]Reference 39
[d]Reference 40
[e]Reference 41
[f]Reference 42
[g]Reference 43

TABLE III: The computed DFT values of equilibrium lattice parameter, bulk modulus, vacancy formation energy, corrected vacancy formation energy are calculated using PAW PBE pseudopotential. The numbers are compared with experimental values as well as data as calculated by Mattson *et al.*

Aluminum	Experiment[a]	Present work	Mattson's work[b]
Eq. lattice parameter	4.04 Å	4.04 Å	4.04 Å
Bulk Modulus	77.3 GPa	77 GPa	78 GPa
Vacancy formation energy	0.68±0.03 eV	0.62 eV	0.63 eV
Vacancy formation energy (corrected)	N/A	0.73 eV	0.78 eV
PP used	N/A	PAW PBE	PAW PBE

[a]Reference 33
[b]Reference 14

TABLE IV: The computed values of exposed surface area as well as corresponding surface corrections are calculated. Exposed surface area are calculated using Mattson's technique (labeled as "MATT") as well as *ab initio* method (labeled as "FP"). Wigner-Seitz radius (r_s) are calculated using Equation 2.

Metals	Electrons per atom (n_e)	Pseudo-potential	XC functional	Wigner-Seitz radius,r_s (Å)	Avg. electron density ($eÅ^{-3}$)	Exposed area due to monovacancy (MATT) ($Å^2$)	Exposed area due to monovacancy (FP) ($Å^2$)	Correction/ Area (FP) ($eV/Å^2$)	Total correction (MATT) (eV)	Total correction (FP) (eV)
Ni	10	PAW	PBE	0.639	0.914	13.766	17.773	0.0383	0.527	0.681
			PW91	0.638	0.918	13.743	17.657	0.0507	0.697	0.895
			LDA	0.621	0.995	13.018	16.895	0.016	0.208	0.270
		US	PW91	0.641	0.907	13.192	17.862	0.0502	0.662	0.897
			LDA	0.622	0.990	13.064	16.886	0.0159	0.208	0.268
Fe	8	PAW	PBE	0.698	0.702	13.362	20.571	0.0301	0.402	0.619
			PW91	0.696	0.708	13.296	18.352	0.0401	0.533	0.736
			LDA	0.676	0.772	12.554	14.112	0.0127	0.159	0.179
		US	PW91	0.704	0.684	13.608	24.292	0.0388	0.527	0.943
			LDA	0.680	0.760	12.692	14.786	0.0126	0.160	0.186
Cr	6	PAW	PBE	0.773	0.516	13.561	19.352	0.0277	0.376	0.439
			PW91	0.770	0.524	13.428	13.553	0.0303	0.407	0.411
			LDA	0.753	0.559	12.848	16.951	0.0095	0.122	0.161
		US	PW91	0.784	0.495	13.924	21.507	0.0289	0.402	0.622
			LDA	0.755	0.555	12.922	16.683	0.0095	0.123	0.158

TABLE V: Corrected values of vacancy formation energies are compared with experimental values. Corrected values using exposed surface area obtained from Mattson's procedure and *ab initio* technique are labeled as "MATT" and "FP" in corresponding columns respectively.

Metals	Experimental Value (eV)	PAW pseudopotential									Ultrasoft pseudopotential					
		PBE			PW91			LDA			PW91			LDA		
		Without Correction	With Correction (MATT)	With Correction (FP)	Without Correction	With Correction (MATT)	With Correction (FP)	Without Correction	With Correction (MATT)	With Correction (FP)	Without Correction	With Correction (MATT)	With Correction (FP)	Without Correction	With Correction (MATT)	With Correction (FP)
Ni	1.78[a] 1.8[b] 1.79[d]	1.45	1.98	2.13	1.4	2.1	2.3	1.68	1.89	1.96	1.41	2.07	2.31	1.7	1.91	1.97
Fe	2±0.2[c]	2.16	2.56	2.78	2.16	2.69	2.89	2.26	2.41	2.43	1.98	2.51	2.92	2.33	2.49	2.52
Cr	2.27[d] 2.0[b]	3.18	3.56	3.63	2.65	3.06	3.06	2.86	2.98	3.02	2.76	3.16	3.38	2.82	2.94	2.98

[a]Reference 37 , [b]Reference 38 , [c]Reference 39 , [d]Reference 40