Energetics of intrinsic point defects in aluminium via orbital-free density functional theory

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ABSTRACT
The formation and migration energies for various point defects, including vacancies and self-interstitials, in aluminium are systematically reinvestigated using the supercell approximation in the framework of orbital-free density functional theory. In particular, the finite-size effects and the accuracy of various kinetic energy density functionals are examined. It is demonstrated that as the supercell size \( N_s \) increases, the finite-size errors asymptotically decrease as \( O(1/N_s^3) \). Notably, the formation energies of self-interstitials converge much more slowly than that of vacancies. With carefully chosen kinetic energy density functionals, the calculated results agree quite well with the available experimental data and those obtained through Kohn–Sham density functional theory, which has an exact kinetic term.

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1. Introduction
Neutrons and other energetic particles produced by nuclear reactions usually induce significant changes in the physical properties of irradiated materials. Since the radiation defects are often very small and hence are not readily accessible to experimental observation, many atomic-, mesoscopic- and continuum-level models have been developed in the past to explain the effects of irradiation on materials [1–4]. Although great achievements have been attained using these empirical models, they all require assumptions regarding the physical laws governing the behaviours of the materials [5]. By contrast, first-principles modelling, which is based on the laws of quantum mechanics, requires only the atomic numbers of the elements as input.

One of the most widely used methods of first-principles modelling is Kohn–Sham density functional theory (KS-DFT) [6,7]. It has been proven that the KS-DFT method can provide reliable information about the structure of nanoscale defects produced by irradiation as well as the nature of the short-range interactions between radiation defects, clustering of defects and their migration pathways [8]. However, the traditional KS-DFT method does not scale linearly,
and it can be applied to treat only about one thousand of atoms even using modern supercomputer [9]. Obviously, it is far from satisfying the requirements for simulating radiation effects in large atomic systems. Orbital-free density functional theory (OF-DFT) is another possible choice for the simulation of radiation effects. Unlike KS-DFT, which uses single-electron orbitals to evaluate the non-interacting kinetic energy, OF-DFT relies on the electron density as the sole variable, in the spirit of the Hohenberg-Kohn theorem [6], and is significantly less computationally expensive. The accuracy of OF-DFT depends upon the quality of the kinetic energy density functional (KEDF) that is used, which is usually based on the linear response of a uniform electron gas. Note that similar to the exchange-correlation density functional (XCDF), the exact form of the KEDF is not known except in certain limits. Currently, the most popular KEDFs are the Wang-Govind-Carter (WGC) [10,11] and Wang-Teter (WT) [12] functionals. Both were designed to reproduce the Lindhard linear response of a free-electron gas [13].

To apply the OF-DFT method to the study of radiation defects in realistic materials, it is essential to evaluate the accuracies of various KEDFs. The formation and migration energetics of typical point defects in the simple metal aluminium are very useful test beds. Indeed, whenever a new KEDF or formulation has been proposed, the vacancy formation energy in Al has always been calculated to perform a comparison between the experimental value and the KS-DFT results [10,12,14–18]. For example, Foley and Madden [16] generalised the WT-KEDF and calculated the relaxed vacancy formation energy in Al using 32- and 108-site cells, and later, Jesson et al. [19] use the same KEDF to calculate the formation and migration energies of various self-interstitials using 108- and 256-site cells. However, the estimated values differed considerably from both the experimental values and the KS-DFT results obtained using the same supercell. Later, Carter’s group [10] proposed the density-dependent WGC-KEDF and also calculated the vacancy formation energy in Al using 4- and 32-site cells. In that work, the estimated value (0.610–0.628) was in very good agreement with the experimental value (∼0.67) and the KS-DFT result (0.626). Subsequently, the same group [20] used various supercells with numbers of sites ranging up to 1372 to calculate the vacancy formation and migration energies. However, it was found that the results calculated using OF-DFT systematically underestimated the measured values and the KS-DFT results by ∼0.2 eV. Recently, Gavini’s group [18,21–23] proposed a non-periodic real-space formulation for OF-DFT and used this formulation to calculate the vacancy formation energy and the energy calculated by relaxing only the ions. The size effect was also considered here. The results were in good agreement with those obtained through OF-DFT calculations using the plane-wave basis [10,20]. Despite the abundant research summarised above on the properties of point defects in Al, relatively little is known regarding OF-DFT investigations of self-interstitials and the corresponding size effect. Thus, it is necessary to systematically calculate the formation and migration
energies of vacancies and various self-interstitials by employing the OF-DFT method with various KEDFs and XCDFs.

The effect of the supercell size on the defect energetics is also a major concern of this work. Because of the periodic boundary condition (PBC) applied in routine DFT calculations using the popular plane-wave basis, there may be cross-boundary effects and defect-defect interactions, and therefore, a different system than the one intended may, in fact, be studied. For KS-DFT, investigation of the size effect is limited by the small size of the system studied and in particular, the imperfection of the Brillouin zone sampling [9,24]. That is to say, the quality of the Brillouin-zone sampling varies smoothly with the number of atoms only for cells of the same type and for defect-containing cell, errors may arise from the Brillouin-zone sampling itself. In contrast, these disadvantages disappear for OF-DFT. For example, Ho et al. [20] found that the formation energy converges to within 3 meV for a $4 \times 4 \times 4$ supercell and that the migration energy converges to within 1 meV for a $3 \times 3 \times 3$ supercell. The finite-size errors from the PBC can also be circumvented using a non-periodic formulation of DFT [18,21]. The corresponding non-periodic cell-size effect on the energetics of vacancies and divacancies in aluminium using OF-DFT was investigated in Refs. [18,22,23,25]. It was revealed that more than 2000 sites are required to obtain a converged value for divacancies.

In the present work, we employ the OF-DFT method with the WGC-KEDF and the WT-KEDF to calculate the formation and migration energies of typical point defects in face-centred cubic (fcc) aluminium. The supercell sizes used for simulation range from $3 \times 3 \times 3$ to $14 \times 14 \times 14$. For comparison, the same energies are also calculated using the KS-DFT method and a $4 \times 4 \times 4$ supercell. The remainder of this paper is organised as follows. The computational methods and details are described in Section 2. In this section, the typical KEDFs used in the calculations are introduced. The detailed results are presented and discussed in Section 3. Section 4 serves as a conclusion.

2. Computational methods and details

According to the Hohenberg-Kohn theorem [6], the ground-state density $n(r)$ of interacting electrons in some external potential $v_{\text{ext}}(r)$ uniquely determines this potential, and the ground-state energy $E$ can be obtained variationally as follows:

$$ E = \min_{\tilde{n}(r)} E_{\text{tot}}[\tilde{n}(r)], $$

(1)

under the constraint that the electron density $\tilde{n}(r)$ is non-negative and normalised with respect to the number of electrons $N$. The minimum is the energy corresponding to the ground-state electron density $n(r)$ for a non-degenerate ground state, which determines all of the properties of the electronic ground state. In the framework of density functional theory, the total energy functional
in Equation (1) can be expressed as

$$E_{\text{tot}}[n(r)] = T_s[n(r)] + E_{\text{xc}}[n(r)] + E_{\text{H}}[n(r)] + \int v_{\text{ext}}(r)n(r)dr,$$

(2)

where $T_s[n(r)]$, $E_{\text{H}}[n(r)]$ and $E_{\text{xc}}[n(r)]$ represent the kinetic energy of the ground state of the non-interacting electrons with density $n(r)$, the Hartree electrostatic energy and the exchange-correlation energy, respectively.

In the framework of the OF-DFT method, it is convenient to build approximately the kinetic term $T_s[n]$ using the KEDF. Here, we adopt the most popular functionals available for this purpose, i.e. the Wang-Govind-Carter (WGC) [10,11] and Wang-Teter (WT) [12] KEDFs. They consist of the Thomas-Fermi (TF) functional [26,27], the von Weizsäcker (vW) functional [28], and a linear response term. In reduced units, the TF-KEDF is given by

$$T_{\text{TF}}[n(r)] = \int n(r)\frac{3}{10}k_F^2[n(r)]dr,$$

(3)

where $k_F[n] = (3\pi^2n)^{1/3}$ is the Fermi wave vector of a uniform electron gas of density $n$ and $\frac{3}{10}k_F^2[n]$ is the mean kinetic energy per electron of such a gas. The vW-KEDF reads

$$T_{\text{vW}}[n(r)] = \frac{1}{8} \int \frac{\nabla n(r)^2}{n(r)}dr,$$

(4)

which can be obtained from a single-orbital occupied system. The response functions of an electronic system are of vital importance for understanding its physical properties, and for a non-interacting electron gas, the correct linear response behaviour was derived analytically by Lindhard [13]. In Lindhard’s theory, the static electric susceptibility in reciprocal space is given by

$$\chi_{\text{Lind}}(q) = -\frac{k_F[n_0]}{\pi^2} \left( \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right), \quad \eta = \frac{|q|}{2k_F},$$

(5)

where $n_0$ is the average electron density. For the TF-KEDF and vW-KEDF, the corresponding susceptibility functions are given by $\chi_{\text{TF}} = -k_F[n_0]/\pi^2$ and $\chi_{\text{vW}} = \chi_{\text{TF}}/(3\eta^2)$, respectively. Clearly, neither the TF-KEDF nor the vW-KEDF can correctly reproduce the linear response behaviour of a uniform electron gas. To remedy this, one must introduce a linear response term; the resulting KEDF is given by

$$T_{\alpha,\beta}^W[n] = T_{\text{TF}}[n] + T_{\text{vW}}[n] + \int \int \{n(r)\}^\alpha w(r, r') \{n(r')\}^\beta drdr'.$$

(6)
For the WT-KEDF \[12\], the linear response kernel \( w(r, r') \) takes the local form

\[
w(r, r') = w_{\alpha, \beta}(r - r') = \mathcal{F}^{-1}\left[-\frac{X_{\text{Lind}}^{-1}(q) - X_{\text{vW}}^{-1}(q) - X_{\text{TF}}^{-1}}{2\alpha\beta n_0^{\alpha+\beta-2}}\right](r - r'), \quad (7)
\]

where \( \mathcal{F}[\cdot](q) \) denotes the Fourier transform, whereas for the WGC-KEDF \[10, 11\], the kernel takes the non-local form

\[
w(r, r') = w_{\alpha, \beta, \gamma}\left(\frac{k_F^\gamma[n(r)] + k_F^\gamma[n(r')]}{2}\right)^{1/\gamma}|r - r'|, \quad (8)
\]

and the exact functional form can be determined by solving a second-order differential equation \[10,11\]. In fact, the WGC-KEDF kernel is evaluated by performing a Taylor series expansion of \( n(r) - n^* \), where \( n^* \) is a reference density that is usually chosen to be the average density \( n_0 \). In this work, the Taylor series expansion is evaluated up to the second order. The exponents \( \alpha \) and \( \beta \) can be either treated as fitting parameters \[12,15,16,19,29–31\] or determined via an asymptotic analysis \[17,32,33\]. In the following, we choose \( \alpha = \frac{5}{6} + \frac{\sqrt{5}}{6} \) and \( \beta = \frac{5}{6} - \frac{\sqrt{5}}{6} \) for the WGC-KEDF and \( \alpha = \beta = \frac{5}{6} \) for the WT-KEDF. The exponent \( \gamma \) is a material-specific adjustable parameter. According to the literature, \( \gamma = 2.7 \) has been found to be optimal for Al \[10,11\].

In the KS-DFT method \[7\], the KEDF can be expressed in terms of the Kohn–Sham orbitals \( \psi_k(r) \):

\[
T_s[n(r)] = \frac{1}{2} \sum_{k=1}^{N} f_k \int |\nabla \psi_k(r)|^2 \, dr, \quad (9)
\]

where the sum is over the \( N \) lowest-energy orbitals \( \psi_k \) and \( f_k \) represents the corresponding occupancy in the orbital \( \psi_k \). The Kohn–Sham orbitals satisfy \( n(r) = \sum_{k=1}^{N} |\psi_k(r)|^2 \). In principle, the expression in Equation (9) is exact, whereas those in Equations (3), (4), and (6) are not.

For KS-DFT, the pseudopotential schemes that are commonly used to represent \( v_{\text{ext}}(r) \) in Equation (2) are usually non-local and can be expressed in terms of Kohn–Sham orbitals. However, because no orbitals are used in OF-DFT, the so-called bulk-derived local pseudopotential (BLPS) \[34,35\] is instead used here to describe the potential \( v_{\text{ext}}(r) \). In both KS-DFT and OF-DFT, the exchange-correlation energy functionals \( E_{\text{xc}}[n] \) in Equation (2) are described using the local density approximation (LDA) \[36\] and the generalised gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) \[37\].

In the present work, we use the PROFESS code to perform the OF-DFT calculations \[38–40\]. Multiple simulation box sizes, corresponding to supercells with dimensions ranging from \( 3 \times 3 \times 3 \) to \( 14 \times 14 \times 14 \), are tested here. Let the supercell size be denoted by \( N_s \); then, the corresponding number of atoms
in the perfect supercell of fcc-Al is given by \(4N_s^3\) and ranges from 108 to 10,976. For electron density optimisation, the kinetic energy cut-off is set to 1200 eV, and the square-root truncated-Newton minimisation method is used with an energy convergence threshold of \(2.72 \times 10^{-5}\) eV. For ion relaxation, dynamic boundary conditions are employed, allowing the cell volume and cell shape to change with the relaxation of the atom positions. In addition, both the conjugate gradient and quickmin algorithms are used, with a convergence threshold of \(2.57 \times 10^{-3}\) eV \(\cdot\) Å\(^{-1}\) for the maximum force component acting on any atom.

For comparison, we also calculate the point defect energies in a \(4 \times 4 \times 4\) supercell using the VASP implementation of the KS-DFT method [41]. The projector augmented-wave (PAW) [42,43] pseudopotential for Al with the \(3s^22p^1\) valence electronic configuration is chosen. The kinetic energy cut-off is taken to be 400 eV, and \(3 \times 3 \times 3\) \(k\)-point meshes based on the Monkhorst-Pack scheme [44] are adopted. Methfessel and Paxton’s smearing method [45] of the first-order is used with a width of 0.1 eV to determine the partial occupancies for each of the Kohn–Sham orbitals. Relaxations are performed by employing the dynamic boundary conditions and using the conjugate gradient and quasi-Newton algorithms with a convergence criterion of 1 meV with regard to the total free energy of the system.

### 3. Results and discussion

#### 3.1. Equilibrium lattice constant

For the bulk properties and energies of several competing phases of bulk Al, Shin et al. [46] have already performed a detailed comparison between the OF-DFT and KS-DFT methods using various exchange-correlation density functionals (XCDFs) and KEDFs. It was found that the OF-DFT results accurately reproduced those obtained using the KS-DFT method. This demonstrates that the OF-DFT method with a reliable BLPS and KEDF is an accurate tool for simulating perfect crystals. Before introducing point defects, we perform structural relaxation on the perfect supercell for fcc-Al to determine the equilibrium lattice constant \(a_0\). In Table 1, we compare the lattice constants of fcc-Al as obtained through various OF-DFT and KS-DFT calculations with the experimental value and the previous theoretical results. The experimental value shown in Table 1 was obtained via extrapolation to 0 K using the polynomial proposed in Ref. [47]. Clearly, all lattice constants obtained using OF-DFT are sufficiently accurate to enable the further investigation of the defect energetics.

#### 3.2. Formation energy of vacancies

Typical defects are now introduced into the fully relaxed supercells, and structural relaxation without any symmetry constraints is performed again for the given supercell to calculate the formation energies. A single vacancy defect is
Table 1. Optimised lattice parameters $a_0$ of fcc-Al as obtained using the KS-DFT and OF-DFT methods with various XCDFs and KEDFs. The experimental value extrapolated to 0 K is also shown for comparison.

| Method          | KEDF  | XCDF | $a_0$ (Å) |
|-----------------|-------|------|-----------|
| KS-DFT          | –     | LDA  | 3.9830    |
| KS-DFT          | –     | GGA  | 4.0387    |
| OF-DFT          | WGC   | LDA  | 3.9725    |
| OF-DFT          | WGC   | GGA  | 4.0579    |
| OF-DFT          | WT    | LDA  | 3.9849    |
| OF-DFT          | WT    | GGA  | 4.0676    |
| KS-DFT [23,35,48] | –     | LDA  | 3.945–3.968 |
| KS-DFT [49]     | –     | GGA  | 4.063     |
| OF-DFT [50]     | Perrot [14] | LDA | 4.06     |
| OF-DFT [50]     | SM [15] | LDA | 3.96     |
| OF-DFT [50]     | WT [12] | LDA | 4.04     |
| OF-DFT [50]     | WGC [10,11] | LDA | 4.03–4.04 |
| OF-DFT [22]     | WGC [10,11] | LDA | 4.022 |
| OF-DFT [23]     | WGC   | LDA  | 3.973     |
| OF-DFT [49]     | WGC   | GGA  | 4.039     |
| OF-DFT [19]     | FM [16] | LDA | 4.0270    |
| Experiment [47] | –     | –    | 4.0315     |

created by eliminating one central atom in the supercell, and the corresponding formation energy is defined as [19]

$$E_v^f = E_{(n-1)\text{Al}} - \frac{n-1}{n}E_{n\text{Al}},$$  \hspace{1cm} (10)

where $E_{(n-1)\text{Al}}$ is the total energy for a supercell containing $(n-1)$Al atoms and one vacancy and $E_{n\text{Al}}$ is the total energy of a perfect aluminium supercell containing $n$ Al atoms. An interstitial defect in Al is generated by adding a single Al atom into the supercell in one of several different interstitial positions around the centre. The corresponding formation energy is given by

$$E_i^f = E_{(n+1)\text{Al}} - \frac{n+1}{n}E_{n\text{Al}},$$  \hspace{1cm} (11)

where $E_{(n+1)\text{Al}}$ is the total energy for a supercell containing $(n)$ Al atoms at lattice sites and one interstitial aluminium atom. Since full relaxation is performed on the perfect and defect-containing systems, $E_v^f$ and $E_i^f$ are the formation energies at constant zero pressure [20,51,52].

We first attempt to test the size dependence of the vacancy formation energy $E_v^f$. The results are shown in Figure 1. The $x$ axis corresponds to the size of the supercell, $N_s$. For a particular defect, the distance between it and its image defect located in a neighbouring cell is given by $d = N_s a_0$. An increase in $N_s$ leads to a larger $d$ and thus reduces the defect-defect interaction. As a consequence, the value of the formation energy asymptotically approaches convergence with increasing $N_s$. This tendency is clearly seen in Figure 1 for the different computational methods. In particular, the WGC-KEDF converges more rapidly than the WT-KEDF, and the LDA-XCDF performs better than...
Figure 1. (colour online) The supercell size dependence of the vacancy formation energy under different combinations of XCDFs and KEDFs. The symbols represent the values calculated using OF-DFT, and the lines represent the fitted curves. The dashed line indicates the optimal supercell size.

The GGA-XCDF. Note that the WGC-KEDF and the LDA-XCDF both perform extremely well and have been recommended in previous publications [20,22,23].

To model the convergence tendency, we use a simple function

\[ E_v^f = \frac{A}{N_s^3} + \frac{B}{N_s^6} + C \]  

(12)

to fit the values of vacancy formation energy. To provide a better understanding of the fitting function, let us note that the main artefact of periodicity for a neutral defect [53] is that the structural distortion around the defect may result in long-range elastic forces, and these elastic effects are expected to behave as \(1/V\), where \(V \propto N_s^3\) is the volume of the supercell. On the other hand, the cell-size effect is also contributed from Friedel oscillations which arise from the local perturbation of point defect and the behaviour is similar. In addition, we have also attempted to use an exponential function of the form \(E_v^f = A \times \exp(-BN_s) + C\) for curve fitting, but we have found the fitting residuals to be slightly larger in this case. The fitted curves are shown in Figure 1, from which the fits appear to be very good. Since the fits always give a positive value of \(B\) in Equation (12), the value of \(C\) may be regarded as the formation energy in the thermodynamic limit \((N_s \to \infty)\). From these results, we observe that the finite-size errors decrease asymptotically as \(O(1/N_s^3)\), and consequently, finite-size scaling can yield a reliable value.

The convergence of \(E_v^f\) with respect to \(N_s\) has already been reported in the previous literature [20,22,23,52]. For the WGC-KEDF, Ho et al. [20] found that the formation energy converges to within 3 meV for a \(4 \times 4 \times 4\) supercell, and this finding has been confirmed by Gavini’s group [22,23,52] and by our calculation (see Figure 1). However, for the WT-KEDF, the convergence of \(E_v^f\) with respect to \(N_s\) is not as rapid as that for the WGC-KEDF. For a convergence criterion
Table 2. Vacancy formation energies $E_f^v$ of fcc-Al as obtained using the KS-DFT and OF-DFT methods with different XCDFs and KEDFs. The experimental value at ‘moderate’ temperature and the previous theoretical results are also shown for comparison.

| Method             | KEDF  | XCDF | $E_f^v$ (eV) |
|--------------------|-------|------|--------------|
| KS-DFT             | –     | LDA  | 0.7291       |
| KS-DFT             | –     | GGA  | 0.6646       |
| OF-DFT             | WGC   | LDA  | 0.7946       |
| OF-DFT             | WGC   | GGA  | 0.7214       |
| OF-DFT             | WT    | LDA  | 1.3458       |
| OF-DFT             | WT    | GGA  | 1.3008       |
| KS-DFT [10,20,52,54–60] | –     | LDA  | 0.66–0.73    |
| KS-DFT [56,58,60]  | –     | GGA  | 0.54–0.55    |
| OF-DFT [16]        | FM [16]| LDA | 0.29         |
| OF-DFT [10,18,20,22]| WGC   | LDA  | 0.48–0.72    |
| OF-DFT [20]        | WGC   | GGA  | 0.387        |
| Experiment [61]    | –     | –    | 0.67 ± 0.03  |

of 1 meV, a supercell size of $8 \times 8 \times 8$ is required for calculating the vacancy formation energy.

The vacancy formation energies of fcc-Al as obtained using the OF-DFT method with various XCDFs and KEDFs are collected and summarised in Table 2. For comparison, the related KS-DFT values for a $4 \times 4 \times 4$ supercell, the previous theoretical results from KS-DFT and OF-DFT, and the experimental value are also shown. Clearly, the formation energies calculated using the OF-DFT method with the WGC-KEDF are close to those of KS-DFT. However, since the kernel in the WT-KEDF is independent of density, it is not suitable for systems in which the electron density varies rapidly, such as those with vacancies or surfaces [10,11]. This finding was reported when the WGC-KEDF was proposed [9,10] and is confirmed here. It is not surprising that the results obtained using the WT-KEDF appear to deviate from the others. In addition, the values obtained using both KS-DFT and OF-DFT with the WGC-KEDF are in good agreement with the experimental value.

### 3.3. Formation energies of self-interstitials

Now let us turn to self-interstitials in fcc-Al. Five types of self-interstitials, including $\langle 100 \rangle$ dumbbell, $\langle 110 \rangle$ dumbbell, $\langle 111 \rangle$ dumbbell, octahedral and tetrahedral interstitials, are considered in the present work. The corresponding formation energies are denoted by $E_{\langle 100 \rangle}^f$, $E_{\langle 110 \rangle}^f$, $E_{\langle 111 \rangle}^f$, $E_{\text{oct}}^f$, and $E_{\text{tet}}^f$, respectively. The relaxed geometry configurations as determined via KS-DFT are shown in Figure 2. The corresponding configurations obtained using the OF-DFT method are very similar and will not be shown here.

Analogously to the vacancy formation energies, as discussed above, the interstitial formation energies also show convergent behaviour with respect to the supercell size. As an example, the formation energies $E_{\langle 100 \rangle}^f$ of a $\langle 100 \rangle$ dumbbell interstitial as functions of $N_i$ and the corresponding fitted curves are shown in Figure 3. Note that the values obtained using small supercell sizes deviate from
Figure 2. (colour online) The geometric configurations of self-interstitials in fcc-Al within a $4 \times 4 \times 4$ supercell: (a) $\langle 100 \rangle$ dumbbell, (b) $\langle 110 \rangle$ dumbbell, (c) tetrahedron, (d) $\langle 111 \rangle$ dumbbell, and (e) octahedron. Note that slices are displayed in (a) and (b). The solid red lines link atoms separated by distances smaller than 2.5 Å; these atoms represent the position of the defect.

Figure 3. (colour online) The supercell size dependence of the formation energy of a $\langle 100 \rangle$ dumbbell interstitial under different combinations of XCDFs and KEDFs. The symbols represent the values calculated using OF-DFT, and the lines represent the fitted curves. The dashed line indicates the optimal supercell size.

the fitted curves and were not used in the fitting process. The convergence rate of $E_{\langle 100 \rangle}^f$ is much slower than that of $E_{\langle 100 \rangle}^v$. For a rough convergence criterion of 5 meV, a supercell size of $7 \times 7 \times 7$ is required to calculate the formation energy of a $\langle 100 \rangle$ dumbbell interstitial. If we focus only on the convergence behaviour, the WGC-KEDF does not perform better than the WT-KEDF, unlike in the case of the vacancy formation energy. Here, the $C$ values in Equation (12)
Table 3. Interstitial formation energies $E_f^I$ (in units of eV) obtained using the KS-DFT and OF-DFT methods with various XCDFs and KEDFs. The subscripts $\langle100\rangle$, $\langle110\rangle$, $\langle111\rangle$, oct and tet indicate the corresponding geometric configurations, as shown in Figure 2. The experimental value was estimated from the experimental formation energies of a Frenkel pair and a vacancy and should therefore be treated as an average.

| Method     | KEDF   | XCDF | $E_{f}^{\langle100\rangle}$ | $E_{f}^{\langle110\rangle}$ | $E_{f}^{\langle111\rangle}$ | $E_{f}^{\text{oct}}$ | $E_{f}^{\text{tet}}$ |
|------------|--------|------|-----------------------------|-----------------------------|-----------------------------|---------------------|---------------------|
| KS-DFT     | –      | LDA  | 2.6073                      | 2.9809                      | 3.1821                      | 2.9485              | 3.2941              |
| KS-DFT     | –      | GGA  | 2.4597                      | 2.7508                      | 3.0183                      | 2.7945              | 3.1072              |
| OF-DFT     | WGC    | LDA  | 2.5867                      |                             |                             |                     |                     |
| OF-DFT     | WGC$^c$| GGA  | 2.6042                      | 2.8867                      | 3.0989                      | 2.8743              | 3.1474              |
| OF-DFT     | WGC     | GGA  | 2.3929                      |                             |                             |                     |                     |
| OF-DFT     | WGC$^c$| GGA  | 2.4210                      | 2.6875                      | 2.8796                      | 2.6733              | 2.9224              |
| OF-DFT     | WT      | GGA  | 2.4268                      | 2.7017                      | 2.8506                      | 2.6684              | 2.8751              |
| OF-DFT     | WT      | LDA  | 2.2953                      | 2.5432                      | 2.6793                      | 2.5313              | 2.7001              |
| KS-DFT [52]| –      | LDA  | 2.9                         | –                           | –                           | 3.1                 | 3.5                 |
| OF-DFT [19]| FM [16] | LDA | 1.579                       | 1.869                       | 1.959                       | 1.790               | 1.978               |
| Exp. [61]  | –      | –    | 3.0$^\dagger$               |                             |                             |                     |                     |

* Here, $\partial^2 w / \partial n^2$ in the WGC-KEDF is set to zero.
† The average value of the formation energy, not the value of $E_{f}^{\langle111\rangle}$.^

as obtained from the exponential fit are again taken as the formation energies in the thermodynamic limit.

Table 3 shows the interstitial formation energies of fcc-Al as obtained using the OF-DFT and KS-DFT methods with various density functionals. The previous theoretical results from KS-DFT [52] and OF-DFT [19] for a $3 \times 3 \times 3$ supercell and the experimental value are also shown for comparison. Note that the experimental value was estimated from the experimental values of the Frenkel pair formation energy, 3.7 eV [61], and the vacancy formation energy, $0.67 \pm 0.03$ eV [61]. We encounter convergence problems when performing OF-DFT calculations with the WGC-KEDF, except in the case of the $\langle100\rangle$ dumbbell configuration. To overcome this difficulty, we repeat the OF-DFT calculations with $\partial^2 w / \partial n^2$ set to 0 in the WGC-KEDF (denoted by WGC$^*$ in the following). The calculated results show that the modified WGC-KEDF leads to slightly larger formation energies.

Surprisingly, the OF-DFT results obtained using the WGC-KEDF are found to reproduce the KS-DFT values extremely well, with errors of less than 0.15 eV. In addition, we find that for the LDA-XCDF, both the OF-DFT and KS-DFT calculations yield

$$E_{f}^{\langle100\rangle} < E_{f}^{\text{oct}} < E_{f}^{\langle110\rangle} < E_{f}^{\langle111\rangle} < E_{f}^{\text{tet}}.$$ 

This is consistent with the experimental finding that a $\langle100\rangle$ dumbbell is the most highly favoured interstitial configuration [62–64]. In addition, the results are of the same order as those calculated using OF-DFT with the FM-KEDF [19] and using KS-DFT [52]. For the GGA-XCDF, the only exception is that $E_{f}^{\langle110\rangle} < E_{f}^{\text{oct}}$ in the KS-DFT case.
Regarding the finding that the $\langle 1\,0\,0 \rangle$ dumbbell configuration is the favoured interstitial configuration, we here attempt to provide a qualitative explanation from the perspective of interatomic interaction. Let us assume that the interstitial formation energy is mainly contributed by the interatomic interaction among atoms separated by very small distances. As seen from Figure 2, the number of atom pairs whose separation distance is smaller than 2.5 Å in the $\langle 1\,0\,0 \rangle$ dumbbell is 1, fewer than in any other self-interstitial-containing system. Therefore, the interstitial formation energy of the $\langle 1\,0\,0 \rangle$ dumbbell system is the smallest, and the $\langle 1\,0\,0 \rangle$ dumbbell configuration is the most stable.

The results of KS-DFT and OF-DFT with the WGC-KEDF are both consistent with the experimental value of 3.0 eV [61]. However, the results of OF-DFT with the WT-KEDF and the FM-KEDF deviate from the experimental value; all of the calculated values for the different geometries are smaller than 3.0 eV. The results [19] obtained using the FM-KEDF differ considerably from our values as well as from the KS-DFT results and the experimental data. Those discrepancies may stem from the local pseudopotentials. For KS-DFT, the values estimated in our work are consistent with the previous theoretical results, and any differences may be the result of different supercells and computational parameters.

3.4. Migration energies of vacancies and $\langle 1\,0\,0 \rangle$ dumbbells

The general migration pathway for a vacancy is that one atom moves towards an adjacent vacancy, eliminating that vacancy and forming a new vacancy. For a $\langle 1\,0\,0 \rangle$ dumbbell, the easiest migration pathway has previously been discussed by Jesson et al. [19]. In this case, one dumbbell atom moves towards an adjacent interstitial site and the other dumbbell atom returns to the lattice site, forming a new $\langle 0\,1\,0 \rangle$ or $\langle 0\,0\,1 \rangle$ dumbbell. The intermediate configurations for the migration of a vacancy and a $\langle 1\,0\,0 \rangle$ dumbbell are depicted in Figure 4. To calculate the migration energy, i.e. the potential barrier for the migration pathway, all possible intermediate configurations are first relaxed, and their energies are then calculated. Then, the migration energy is given by the difference between the maximum total energy of the intermediate configurations and the total energy of the initial configuration. For KS-DFT with the LDA-XCDF, the intermediate atomic configurations for the migration of a vacancy and a $\langle 1\,0\,0 \rangle$ dumbbell with the maximum total energy are shown in Figure 4.

The migration energies also show convergent behaviour with respect to the supercell size $N_s$. In Figure 5, the supercell size dependence of the vacancy migration energy $E^m_v$ is shown. The convergence rate of $E^m_v$ is not as good as that of $E^f_v$. In particular, it is difficult to achieve convergence for $E^m_v$ using the OF-DFT method with the WT-KEDF, which again confirms that the WT-KEDF is not suitable for describing systems with vacancy defects. In addition, the convergence of $E^m_{\langle 1\,0\,0 \rangle}$ is not as good as that of $E^m_v$. Thus, in the following OF-DFT calculations, we use only the results from the $14 \times 14 \times 14$ supercell.
Figure 4. (colour online) The intermediate atomic configurations for vacancy migration (left) and ⟨100⟩ dumbbell migration (right). For the migrating atoms, the arrows, red dotted circles and blue circles schematically represent the migration direction and the positions before and after migration, respectively.

Figure 5. (colour online) The supercell size dependence of the vacancy migration energies calculated using different combinations of XCDFs and KEDFs. The symbols represent the values calculated using OF-DFT, whereas the lines represent the fitted curves.

Table 4 shows the migration energies of a vacancy and a ⟨100⟩ dumbbell as obtained using the OF-DFT and KS-DFT methods. We also show the experimental values and the available theoretical results for comparison. The vacancy migration energy $E_v^m$ that is obtained using the OF-DFT method with the WGC-KEDF well reproduces that obtained using the KS-DFT method as well as the experimental value. As illustrated above, because of the density-independent kernel, the $E_v^m$ values obtained via OF-DFT with the WT-KEDF cannot reproduce the KS-DFT results and are also in poor agreement with the experimental values.

For the ⟨100⟩ dumbbell migration energy $E_{⟨100⟩}^m$, the OF-DFT results differ from the KS-DFT results. However, the $E_{⟨100⟩}^m$ values obtained using the OF-DFT method are in close agreement with the experimental results, whereas the KS-DFT results are not. In addition, the deviations of the OF-DFT results from the previous theoretical results are acceptable.
Table 4. The migration energies (in units of eV) of a vacancy and a ⟨100⟩ dumbbell as obtained using the OF-DFT and KS-DFT methods with various density functionals.

| Method   | KEDF | XCDF | $E_{mv}^m$ | $E_{m}^m$ (100) |
|----------|------|------|------------|-----------------|
| KS-DFT   | –    | LDA  | 0.5234     | 0.2130          |
| KS-DFT   | –    | GGA  | 0.4904     | 0.2179          |
| OF-DFT   | WGC  | LDA  | 0.5846     | –†              |
| OF-DFT*  | WGC  | LDA  | 0.6251     | 0.1168          |
| OF-DFT   | WGC  | GGA  | 0.5569     | –†              |
| OF-DFT   | WGC  | GGA  | 0.5964     | 0.1101          |
| OF-DFT   | WT   | LDA  | 0.3135     | 0.1119          |
| OF-DFT   | WT   | GGA  | 0.3041     | 0.1041          |
| OF-DFT [19] | FM [16] | LDA | –          | 0.084           |
| OF-DFT [20] | WGC | LDA  | 0.42       | –               |
| Exp. [61] | –    | –    | 0.61 ± 0.03| 0.115 ± 0.025   |

*Here, a modified WGC-KEDF is used with $\partial^2w/\partial n^2 = 0$.
†In this scheme, the electron density does not converge.

4. Conclusion

In summary, the OF-DFT method combined with the WGC-KEDF and the WT-KEDF was employed to calculate the formation energies and migration energies of typical point defects in fcc-Al supercells consisting of up to 10,976 atoms. The finite-size errors arising from the supercell approximation were examined, and it was found that they could be corrected using finite-size scaling methods. The convergence of the interstitial formation energies is much slower than that of the vacancy formation energy. Our cell-size study of ⟨100⟩ dumbbell interstitials shows that the formation energy converges to within 5 meV for a 7 × 7 × 7 supercell. We compared the accuracies achieved using commonly applied KEDFs. We found that when the WGC-KEDF is used, the calculated results agree quite well with the more accurate data obtained via KS-DFT calculations. Sometimes, however, it is not easy to achieve convergence with the WGC-KEDF. Usually, we can apply a slightly modified WGC-KEDF in which $\partial^2w/\partial n^2 = 0$ to overcome this obstacle. By contrast, the WT-KEDF tends to yield incorrect estimates, especially for vacancies [10,11], and is not suitable for the simulation of defect-containing systems.

Our results suggest that with a carefully chosen KEDF, the accuracy of OF-DFT calculations will be comparable to that of KS-DFT calculations, which are more demanding in terms of computer resources. Therefore, the application of the OF-DFT method with the WGC-KEDF shows promise for studying large-scale systems with defects, such as the collision cascade process in irradiated materials.

Disclosure statement

No potential conflict of interest was reported by the authors.
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