Density-functional embedding using a plane-wave basis

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The constrained electron density method of embedding a Kohn-Sham system in a substrate system (first described by P. Cortona, Phys. Rev. B 44, 8454 (1991) and T.A. Wesolowski and A. Warshel, J. Phys. Chem 97, 8050 (1993)) is applied with a plane-wave basis and both local and non-local pseudopotentials. This method divides the electron density of the system into substrate and embedded electron densities, the sum of which is the electron density of the system of interest. Coupling between the substrate and embedded systems is achieved via approximate kinetic energy functionals. Bulk aluminium is examined as a test case for which there is a strong interaction between the substrate and embedded systems. A number of approximations to the kinetic-energy functional, both semi-local and non-local, are investigated. It is found that Kohn-Sham results can be well reproduced using a non-local kinetic energy functional, with the total energy accurate to better than 0.1 eV per atom and good agreement between the electron densities.

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I. INTRODUCTION

For the past two decades Density Functional Theory (DFT) has been one of the most powerful tools for the \textit{ab initio} calculation of the physical and chemical properties of materials. Methods based on DFT make efficient use of computational resources, hence can generally deal with larger and more complex systems than other \textit{ab initio} methods. They also provide a simple interpretation of much of the many-electron physics of materials in terms of ideas based on the electron gas. A number of implementations of DFT exist, which essentially differ in the approach taken to approximating the unknown density functional that describes the contribution to the electronic energy that is \textit{not} due to the external potential.

The most successful of these methods is the approach first derived by Kohn and Sham [4], which uses DFT to identify the interacting electrons with a non-interacting electron gas, and then solves for the non-interacting electron system. Most of the energy of the system is evaluated exactly, with only a relatively small exchange-correlation contribution requiring approximation. In addition, the exchange-correlation part of the functional can be well approximated by a simple analytic form, hence this has become the workhorse of accurate DFT [3]. There is one main disadvantage that concerns us here. Within the standard Kohn-Sham approach the electron density is expressed as the electron density of a non-interacting, many-electron system, by obtaining the eigenstates of these non-interacting electrons; this requires $O(N^3)$ operations where $N$ is the number of electrons present in the system. It is this scaling behaviour that limits the size of system that the Kohn-Sham method can be applied to (currently less than around 1000 atoms).

A more direct and computationally cheaper approach is to minimise the total energy functional with respect to variations in the electron density, $\rho(r)$ (eg Wang et al [6]). In this form the cost of finding the minimum of the total energy does not depend on $N$ provided the non-interacting kinetic energy functional $T_s[\rho]$ is available as an explicit functional of the electron density. Unfortunately, this functional is not known, hence a direct minimisation procedure must employ approximate forms of the kinetic energy functional as well as the exchange-correlation energy. Approximate expression are available, but as $T_s[\rho]$ is generally an order of magnitude greater than the exchange-correlation energy they are generally not of sufficient accuracy for structural optimisation, let alone chemical calculations. Another deficiency is that there is no obvious way of applying the familiar non-local pseudopotentials of Kohn-Sham methods to these direct minimisation methods, although indirect methods have been proposed by Watson et al [7], Anata and Madden [8] and Shah et al [9].

Other methods have been investigated, such as a path integral formulation of Kohn-Sham theory [10], and several approaches which formulate DFT as a 1st order reduced density matrix theory [2-11]. The latter formulation takes advantage of the ‘nearsightedness’ (see Kohn [12]) of the density matrix to solve for the ground state energy as an $O(N)$ problem, with the non-interacting kinetic energy functional evaluated exactly (eg Baroni and Giannozzi [13], Hernández et al [14], Ordejon [15], and a recent review by Goedcker [16]). Although \textit{ab initio} $O(N)$ approaches of this form are successful, they are currently limited to insulators as the density matrix is long-ranged for systems with no band gap.

A middle ground between the Kohn-Sham method and direct energy functional minimisation can be found via ‘embedding methods’, and this is the approach considered in this paper. In many cases the system we are interested in may be divided into two regions, $I$ and $II$. 

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Region $II$ is largely the same as a more simple system that may easily be solved for, whereas region $I$ is where the interesting physics occurs. An example would be a defect in a crystal - region $II$ would be a bulk crystal, and region $I$ a small volume surrounding the defect. There is an obvious computational advantage in solving for region $II$ first, and then solving for region $I$ taking into account the influence of region $II$ in some way. This ‘embedding’ approach has received a great deal of attention, and a large number of methods have been presented in the literature. No attempt is given to review all of these, but we refer to publications that describe general classes of methods. For the main part these differ in the space in which region $I$ and region $II$ are defined. Inglesfield [17] defined these regions in real space and constructed an exact embedding scheme that requires a knowledge of the Green function of the substrate (region $II$), which is often prohibitively costly to calculate. Regions $I$ and $II$ can also be defined more generally in Hilbert space, as described by Fisher [18]. Another approach is discussed by Gutdeutsch et al [19, 20], where the $1^{st}$ order reduced density matrix is partitioned. All of these schemes are, to a greater or lesser extent, based on a wavefunction description of the embedding process.

Here we apply a different procedure, first described by Cortona [21] and Wesolowski and Warshel [22], that carries out the embedding entirely at the density functional level. The essential idea is to express the total energy of the system in terms of two Kohn-Sham like systems with densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ (corresponding to regions $I$ and $II$), where the total electron density is given by $\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})$. This total energy is then minimised by varying only the electron density $\rho_1(\mathbf{r})$, corresponding to fewer electrons than the whole system, and so a cheaper calculation. Potential applications of this method include defects in crystals, or adsorbates on surfaces, since once a solution for the substrate is available the remainder of the calculation would only involve the Kohn-Sham representation of the electrons in the immediate vicinity of the defect or adsorbate. This partially frozen electron density method has been implemented by Cortona [21], Wesolowski et al [22, 23, 24, 25] and (in a slightly different context) Govind et al [26] in a form that describes the coupling between the two subsystems via approximate kinetic energy functionals. A localised set of basis functions was used in each case.

In this paper this procedure is implemented within a plane-wave pseudopotential framework [8]. We investigate the approach for metallic systems where the electrons in regions $I$ and $II$ are strongly interacting, whereas past applications have focused on insulating systems and a relatively weak interaction. Our goal is to develop an embedding approach accurate enough, and computationally cheap enough, to aid the investigation of large scale defect and adsorbate systems. As a preliminary to this we test and analyse the approach by constructing a four atom cell of bulk fcc aluminium by embedding one cubic sub-lattice of atoms within three others. Sections II and III describe the implementation of the method, with approximate kinetic energy functionals described from the viewpoint of a plane-wave basis. Subsection IV A presents the results of the method applied to bulk fcc aluminium, with a number of different kinetic energy functionals. In subsection IV B a modified form of the method is applied in order to analyse the source of errors, again for different functionals. Another important issue in the direct application of DFT methods is the inclusion of non-local pseudopotentials. In subsection IV C we present and justify the assumptions that must be made in order to employ non-local pseudopotentials within the embedding scheme. Rydberg atomic units are used throughout unless otherwise stated.

II. PARTIALLY FROZEN ELECTRON DENSITY

We begin with the familiar Hohenberg-Kohn total energy functional $E[\rho]$, expressed in the Kohn-Sham form [3]

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} \quad (1)$$

where $T_s[\rho]$ is the non-interacting kinetic energy functional, $J[\rho]$ is the Hartree energy, $V_{ext}$ is the local external potential (for the systems considered here it is given by the sum of local pseudopotentials at each atomic site) and $E_{xc}[\rho]$ is the exchange-correlation energy, including the kinetic-correlation contribution. In the standard Kohn-Sham methodology the functional derivative of Eq. (1) is taken with the total number of electrons constrained to be constant. By setting this equal to zero an Euler-Lagrange equation is obtained, which is identified with the Euler-Lagrange equation for a system of non-interacting electrons in a specific external potential. Solving for this ‘reference’ system to yield the same electron density as the interacting system is the essence of the Kohn-Sham implementation of density functional theory, and results in the electron density that gives the correct minimum of Eq. (1), the ground state energy.

The partially frozen electron density method breaks down this same functional into two non-interacting gases. The electron density of the system, $\rho(\mathbf{r})$, is divided into two components so that $\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})$. One of these components (in what follows, $\rho_1(\mathbf{r})$) is taken to represent a part of the system that is expected to change very little (this will be qualified further on): the substrate. This is kept constant, and in what follows is obtained from a Kohn-Sham calculation so the kinetic energy $T_s[\rho_1]$ is known accurately. The total energy functional is then expressed in terms of the kinetic energy functional of $\rho_1(\mathbf{r})$ and an ‘embedding kinetic energy’ term, $T_s^{add}[\rho_1,\rho_2] + T_s[\rho_2]$ that takes into account the influence of the rest of the system. This gives the total
energy as \[21, 22\]

\[
E[\rho] = T_s[\rho_1] + T_n[\rho_1, \rho_2] + T_v[\rho_2] + J[\rho] + E_{\text{ext}}[\rho] + \int V_{\text{ext}}(r)\rho(r)d^3r \tag{2}
\]

where the non-additive part of \(T_s[\rho], T_n^{\text{add}}[\rho_1, \rho_2],\) is defined as

\[
T_n^{\text{add}}[\rho_1, \rho_2] = T_s[\rho_1 + \rho_2] - T_s[\rho_1] - T_s[\rho_2]. \tag{3}
\]

Minimising Eq. (2) with respect to variations in \(\rho_1(r)\) only, with the substrate density \(\rho_2(r)\) constant, and a constraint of constant total number of electrons in \(\rho_1(r)\), results in the Euler-Lagrange equation

\[
\frac{\delta T_s[\rho_1]}{\delta \rho_1} + \frac{\delta T_n^{\text{add}}[\rho_1, \rho_2]}{\delta \rho_1} + V_{\text{KS}}[\rho; r] = \mu \tag{4}
\]

where \(\mu\) is an arbitrary constant reflecting the fact that for a fixed number of electrons the functional derivative is defined to within an additive constant only. In the same manner as for the Kohn-Sham case, this leads to the \(\rho_1(r)\) being the solution of the ‘Kohn-Sham’ equations associated with Eq. (4) at self consistency, but with an effective potential given by

\[
V_{\text{eff}}[\rho; r] = V_{\text{KS}}[\rho; r] + \frac{\delta T_n^{\text{add}}[\rho_1, \rho_2]}{\delta \rho_1} = V_{\text{KS}}[\rho; r] + \left(\frac{\delta T_s[\rho_1 + \rho_2]}{\delta \rho_1} - \frac{\delta T_s[\rho_1]}{\delta \rho_1}\right) \tag{5}
\]

If an exact expression for the kinetic energy functional was available this prescription would provide a ground state energy and electron density exactly equivalent to the Kohn-Sham scheme for the total system, with one additional limitation. Since \(\rho_1(r)\) takes the form

\[
\rho_1(r) = \sum_i w_i|\psi_i(r)|^2 \tag{6}
\]

it is positive, hence the trial densities that are searched to minimise the total energy in Eq. (1) satisfy \(\rho(r) \geq \rho_2(r)\), and the true ground state energy and density is obtained only if the ground state density satisfies this inequality. In practise \(\rho_2(r)\) is chosen such that this is not a significant restriction, and this is true for the test cases considered in section IV. This constraint may also be relaxed by applying a ‘Freeze and Thaw’ procedure, as discussed at the end of subsection IV.B

Since \(\rho_2(r)\) is taken as already known, this method of obtaining the electronic structure need only solve for the electrons present in \(\rho_1(r)\), a smaller number (in many cases considerably smaller) than is present in the entire system. However, in order to apply this approach the term \(T_n^{\text{add}}[\rho_1, \rho_2]\), or non-additive kinetic energy \[27, 28\], and its functional derivative in Eq. (2) and Eq. (5) are required. Since no explicit form is available approximate kinetic energy functionals are employed in Eq. (3) to provide an approximate non-additive kinetic energy functional. To clarify, we approximate all of the functionals on the RHS of Eq. (3), whereas in Eq. (2) the functionals \(T_s[\rho_1]\) and \(T_v[\rho_2]\) are exact. This approximation to the non-additive kinetic energy is the only additional source of error introduced by the method, but \(T_n^{\text{add}}\) is expected to be far smaller than the total kinetic energy (it is zero if \(\rho_1(r)\) and \(\rho_2(r)\) do not overlap) for most reasonable divisions of the electron density, and it could be hoped that some error cancellation will occur.

The non-additive kinetic energy has been investigated as a test of the quality of a number of kinetic energy functionals by Lacks and Gordon [27], who compared \(T_n^{\text{add}}\) for Helium and Neon calculated from approximate functionals with Hartree-Fock results. They conclude that the fractional error of \(T_n^{\text{add}}\) is greater than for the kinetic energy of the whole system, implying that for weakly interacting subsystems the error cancellation is limited. Whether this is the case for more strongly interacting subsystems and for the functionals applied here will have a direct influence on the accuracy of our results. In addition it should be remembered that even if the approximate functional gives the correct kinetic energy for the true density, this may not be a minimum of the total energy with respect to variations in the density.

### III. APPROXIMATE KINETIC ENERGY FUNCTIONALS

Approximations to the kinetic energy functionals are used to construct \(T_n^{\text{add}}[\rho_1, \rho_2]\) in Eqs. (2-5). Many are available in the literature (eg Thakkar [29], Wang et al[6], García-González et al [30], Herring [31]), and these have been assessed in a number of environments ranging from isolated atoms to bulk systems to molecular interactions and surfaces. The majority of these assessments investigate the ability of the functionals to reproduce accurate kinetic energies from accurate electron densities calculated by other means. A smaller number of studies have examined the ability of approximate functionals to produce accurate electron densities and energies when the total energy is minimised using the functionals themselves, and little work has been published on the success of these approximations in reproducing accurate functional derivatives. We have therefore chosen to examine a range of functionals.

Although an analytic gradient expansion exists for \(T_s[\rho]\), convergence cannot be achieved for systems where the density decays exponentially [2]. This has been attributed to the expansion taking the form of an asymptotic series, as described by Pearson and Gordon [32], although this has not been shown analytically. In order to overcome this difficulty in improving the local density approximation (LDA) to \(T_s[\rho]\), many authors have taken a similar approach to the Generalised Gradient Approximation (GGA) to the exchange-correlation functional, by carrying out a partial re-summation via an enhancement
The kinetic energy is approximated by

$$T_{s}^{app}[\rho] = \frac{3}{5}(3\pi^2)^{\frac{2}{3}} \rho \rho F(t) dR$$ (7)

where

$$t = \frac{|\nabla \rho|^2}{\rho^{\frac{3}{2}}}$$, (8)

hence the kinetic energy is expressed as a semi-local functional of the electron density and its gradient. The functional derivative of a general semi-local density functional

$$G[\rho] = \int g(\rho, \nabla \rho, \nabla^2 \rho, \cdots) d^3R$$ (9)

is given by [3]

$$\frac{\delta G}{\delta \rho} = \frac{\partial g}{\partial \rho} - \nabla \cdot \left( \frac{\partial g}{\partial \nabla \rho} + \nabla^2 \frac{\partial g}{\partial \nabla^2 \rho} \right) + \cdots$$ (10)

which may be truncated at second order for the functional given in Eq. (7), since the kernel is a function of $\rho$ and $\nabla \rho$ only.

The direct application of Eq. (10) to the semi-local functional, Eq. (7), yields

$$\frac{\delta T_{s}^{app}[\rho]}{\delta \rho} = \frac{1}{5}(3\pi^2)^{\frac{2}{3}} \left[ 5\rho \dot{\rho} F(t) - 6 \frac{\nabla^2 \rho}{\rho} F'(t) - 2 \frac{|\nabla \rho|^2}{\rho^2} (F'(t) - 8t F''(t)) - 12t F''(t) \frac{\nabla \rho \cdot \nabla |\nabla \rho|}{\rho |\nabla \rho|^2} \right]$$ (11)

an unwieldy expression that involves highly non-linear terms. With a plane-wave basis difficulties arise due to $\rho(r)$ being defined on a real space grid, with gradients conventionally obtained via the Fast Fourier Transform (FFT). Since Eq. (11) is non-polynomial in $\rho(r)$ it cannot be represented by a finite Fourier space, and using any finite space results in aliasing errors. For example, the term $\nabla \rho \cdot \nabla |\nabla \rho|$ results in particularly large errors, and if Eq. (11) is applied directly this causes errors in the resulting potential to propagate through further iterations, preventing convergence.

Exactly this problem manifests itself in the application of the GGA with a plane-wave basis, as discussed by White and Bird [32]. In this case convergence is also affected, though not as severely due to the exchange-correlation energy being an order of magnitude smaller than the kinetic energy. We follow the same approach as White and Bird to find a more stable expression for the kinetic energy functional derivative. The functional is discretised as a sum of contributions at each real space grid point,

$$T_{s}^{app}[\rho] = \frac{3}{5}(3\pi^2)^{\frac{2}{3}} \frac{\Omega}{N} \sum_{R} \dot{\rho}_R F(t_R)$$ (12)

where $\Omega$ is the volume of the unit cell, $N$ is the number of grid points, and the subscript $R$ denotes the quantity at the grid point $R$. The ‘functional derivative’ (in fact a total derivative) can then be written in terms of the partial derivative of Eq. (12) with respect to $\rho_R$ and $\nabla \rho_R$, which are considered as independent variables. This yields the expression

$$\left. \frac{\delta T_{s}^{app}[\rho]}{\delta \rho} \right|_R = \frac{3}{5}(3\pi^2)^{\frac{2}{3}} \left[ \frac{5}{3} \dot{\rho}_R^2 F(t_R) - \frac{8}{3} \frac{|\nabla \rho_R|^2}{\rho^2} F'(t_R) - \nabla \cdot \left( \frac{2}{3} \frac{\nabla \rho_R}{\rho R} F'(t_R) \right) \right]$$ (13)

which is analytically equivalent to Eq. (11) in the limit $N \rightarrow \infty$. Expression (13) for the functional derivative is applied in our calculations, with all gradients calculated via the FFT, and is found to remove the instability inherent in Eq. (11).

It is important to note that although Eq. (13) defines the functional derivative in a manner consistent with a finite real space grid, it does not ensure that an accurate representation of the functional derivative is obtained for a given electron density. This is immediately apparent if an exponentially decaying electron density is considered. In this case the second and third terms in Eq. (13) should result in the expressions $|\nabla \rho_R|^2$ and $|\nabla \rho_R|^2$ being constant due to a cancellation of the exponentials. However, since the numerator in both these terms will in fact be the gradient of a trigonometric representation of the electron density an exact cancellation will not occur, and for small values of $\rho_R$ errors in these terms (and the resulting functional derivative) will not be small. This is found to prevent convergence if the derivative of $F(t)$ in Eq. (13) is large, but has no effect for the functionals considered here.

A number of enhancement factors available in the literature [24, 29] were investigated (specifically the Thomas-Fermi approximation and 1st order gradient expansion [23], and the functionals constructed by Thakkar [21], Vitos et al [34], DePristo and Kress [35], On-Yang and Levy [36], Lee et al [37], Perdew and Wang [38–40] and Lembarki and Chermette [41]), but their overall behaviour was found to be similar. We therefore present results for two enhancement factors only. The first is that of Perdew and Wang, $F_{PW86}$ [39],

$$F_{PW86}(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{\frac{1}{3}},$$ (14)

where

$$s = \frac{1}{2(3\pi^2)^{\frac{1}{2}}} t^{\frac{1}{2}}.$$ (15)

We choose this enhancement factor since Lacks and Gordon [27] found it gave the best approximation to the non-additive kinetic energy of a number of related functionals. The second enhancement factor is

$$F_{TF-\lambda W}(s) = 1 + \frac{5}{3}s^2,$$ (16)
which for \( \lambda = 0 \) is the Thomas-Fermi (TF) approximation and for \( \lambda = \frac{1}{2} \) the gradient expansion truncated at first order. The parameter \( \lambda \) is taken as a free parameter in order to optimise the results of the calculations (this is not a completely empirical approach and some theoretical justification is available \[2, 42\]).

A number of more general non-local approximations to the kinetic energy functional are available, such as local density scaling \[42\] and weighted density approximations (eg Chacón et al \[44\], García-González et al \[50\]). Although these approaches are accurate they are computationally expensive, hence we choose a simpler form which has been found to accurately reproduce energies and densities for some bulk systems \[6\]. This functional is from the family of approximations introduced by Wang and Teter \[45\], Perrot \[46\] and by Smargiassi and Madden \[47\], summarised and generalised by Wang et al \[6\]. These take the form

\[
T_{\alpha}^{nl} = \frac{3}{5} (3\pi^2)^{\frac{2}{3}} \int \rho^\frac{5}{3} \mathbf{d}^3 \mathbf{r} - \int \rho^\frac{2}{3} \nabla^2 \rho^\frac{5}{3} \mathbf{d}^3 \mathbf{r} + \int \rho^\alpha \omega_\alpha(\mathbf{r}) \rho^\alpha \mathbf{d}^3 \mathbf{r} \quad (17)
\]

where the first term is the TF functional, the second term is the von Weizsacker (vW) functional and the third term is defined such that the entire functional has the correct linear response for a homogenous, non-interacting electron gas. A number of different values have been proposed for the parameter \( \alpha \), each with its own justification as discussed by Wang et al \[6\]. For a plane-wave representation of \( \rho(\mathbf{r}) \) Eq. (17) takes the form

\[
T_{\alpha}^{nl} = \Omega \sum_\mathbf{g} \frac{3}{5} (3\pi^2)^{\frac{2}{3}} \rho_\mathbf{g}^\frac{5}{3} \rho_\mathbf{g}^\frac{5}{3} + \rho_\mathbf{g}^\frac{2}{3} \rho_\mathbf{g}^\frac{2}{3} + \rho_\mathbf{g}^\alpha \omega_\mathbf{g}(\mathbf{g}) \rho_\mathbf{g}^\alpha \quad (18)
\]

where the powers of the electron density are taken before transformation to reciprocal space, and \( \Omega \) is the volume of the unit cell. The linear response correction, \( \omega_\mathbf{g}(\mathbf{g}) \) is given by

\[
\omega_\mathbf{g}(\mathbf{g}) = -\frac{k_f^2}{3\alpha^2 \rho_0^{2\alpha-1}} - \frac{1}{4\alpha^2 \rho_0^{2\alpha-1}} g^2 - \frac{1}{2\alpha^2 \rho_0^{2(\alpha-1)}} \chi_{Lind}(\mathbf{g}) \quad (19)
\]

with \( \chi_{Lind} \) the Lindhard susceptibility function in reciprocal space,

\[
-\frac{1}{\chi_{Lind}} = \frac{2\pi^2}{k_f} \left( \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta^2}{1 - \eta^2} \right| \right)^{-1} \quad (20)
\]

where \( k_f = (3\pi^2 \rho_0)^{\frac{1}{3}} \) is the Fermi vector for the average electron density \( \rho_0 \), and \( \eta = \frac{g}{2k_f} \). The functional derivative can be obtained by writing Eq. (17) as a discrete sum (double sum for the linear response correction) over the real space grid, in the same manner as White and Bird’s treatment of the semi-local functionals. Introducing an infinitesimal change in \( \rho(\mathbf{r}) \) at a grid point results in

\[
\frac{\delta T_{\alpha}^{nl}}{\delta \rho(\mathbf{r})} = \Omega \left[ (3\pi^2)^{\frac{2}{3}} \rho_\mathbf{g}^\frac{5}{3}(\mathbf{r}) + \rho^{-\frac{2}{3}}(\mathbf{r}) \sum_\mathbf{g} g^2 \rho_\mathbf{g}^\frac{2}{3} e^{i\mathbf{g} \cdot \mathbf{r}} + 2\alpha \rho_\mathbf{g}^{\alpha-1}(\mathbf{r}) \sum_\mathbf{g} \omega_\mathbf{g}(\mathbf{g}) \rho_\mathbf{g}^\alpha e^{i\mathbf{g} \cdot \mathbf{r}} \right]. \quad (21)
\]

Equation (21) was found to be stable for \( \alpha = \frac{1}{2} \), but became unstable for other values. This behaviour can be ascribed to the fact that in the limit of \( g \to 0 \) Eq. (17) gives the exact second order gradient expansion only for \( \alpha = \frac{1}{3} \). For all other values this not the case, hence the convergence problems associated with exponentially decaying, low electron density regions described earlier become significant.

IV. EMBEDDING TESTED ON BULK FCC ALUMINUM

A. All terms of \( T_{\alpha}^{nl} \) approximate

To investigate this partially frozen density approach we examine fcc aluminium with a 4 atom cubic unit cell. The 3 face-centred atoms are taken to be the substrate system, and this structure is solved to provide \( \rho_2(\mathbf{r}) \) and \( T_\alpha(\mathbf{r}) \). A plane-wave basis pseudopotential approach is used, with a lattice constant of \( a_0 = 4.05\AA \), a plane-wave cut-off of 200 eV, 35k points in the irreducible wedge of the Brillouin zone, and the Goodwin-Needs-Heine \[48\] local pseudopotential (a non-local pseudopotential is considered in subsection IV C). Exchange-correlation is described by the LDA.

Once this substrate is constructed the embedded Kohn-Sham calculation is carried out as a standard plane-wave basis calculation, but with the trial potential given by Eq. (15) and the total energy given by Eq. (12). The non-additive kinetic energy in Eq. (12) is given by Eq. (13) with all of the terms on the RHS approximate. The unit cell, Brillouin zone sampling and other parameters of the calculation are chosen to be the same as the substrate calculation. It should be made clear that for the substrate calculation we are solving for the lattice of 3 face centred atoms and their accompanying electrons, but for the embedded calculation we are solving for the entire fcc system, but only the electrons associated with the embedded (corner) atom are provided with a Kohn-Sham representation.

We discuss results for 3 approximate functionals. Equation (10) was applied with \( \lambda = \frac{1}{3} \) (denoted \( T_{TF, \frac{1}{3}} \)), since this value was found to provide a useful compromise between accuracy of the value of the functional itself and the functional derivative. We also employ Eq. (14) (\( T_{PW66} \)) and the non-local linear response corrected functional, Eq. (17), with \( \alpha = \frac{1}{2} \) (denoted
TABLE I: Total energy per atom $E$, and errors in energy $\Delta E$ and electron density. Results obtained with embedding scheme described in subsection IV A.

| Functional | $E$/eV | $\Delta E$/eV | $R$/% | $\times 10^{-3}$ Å$^{-3}$ |
|------------|--------|---------------|-------|---------------------------|
| $T_{TF-\frac{1}{2}W}$ | $-58.722$ | $-0.392$ | $4.206$ | $28.750$ |
| $T_{PW86}$ | $-58.052$ | $0.277$ | $6.390$ | $31.491$ |
| $T_{nloc}$ | $-58.337$ | $-0.008$ | $4.614$ | $20.051$ |
| Kohn Sham | $-58.329$ | | | |

In Table I the total energy per atom of the embedded calculations are given, together with the result of a full Kohn-Sham calculation carried out with the same basis and pseudopotential. $T_{nloc}$ gives by far the best result for the total energy, although the extreme accuracy of this value is probably spurious since similar systems consistently provide errors of order $\sim 0.1$ eV/atom. The total energy for the other functionals is not as accurate, and results for other semi-local functionals that are not given here are similar or worse.

Fig. 1a, Fig. 1b and Fig. 1c show the electron density obtained using the $T_{TF-\frac{1}{2}W}$, $T_{PW86}$ and $T_{nloc}$ functionals respectively. These figures show the electron density along a line in the [111] direction between two embedded atoms on the corners of the cubic unit cell. Table I gives the error in the electron density, compared with the Kohn-Sham results, over the whole unit cell. This is quantified as the peak error and the average absolute error, $R$, given by

$$R = \int |\rho(r) - \rho^{KS}(r)|d^3r/\int \rho^{KS}(r)d^3r,$$

where $\rho^{KS}(r)$ is the Kohn-Sham electron density. From these results it is apparent that the electron densities show the correct behaviour, reproducing the structure of the Kohn-Sham electron density reasonably well. However, errors appear near the atomic sites of the embedded atoms as well as in the region where $\rho_1(r)$ and $\rho_2(r)$ have the greatest overlap. Considering the errors in both the electron density and total energy, $T_{nloc}$ provides the most accurate reproduction of the Kohn-Sham results.

B. One term of $T_{\text{add}}$ approximate

In this section we approximate the non-additive kinetic energy in a form that represents the kinetic energy of the entire system as an approximate kinetic energy functional. However, the densities $\rho_1(r)$ and $\rho_2(r)$ are still represented as Kohn-Sham systems. This corresponds to the many applications of approximate kinetic energy functionals to the direct minimisation of the total energy function (see Goedecker [10]) with no Kohn-Sham representation.

![FIG. 1: Electron density in [111] direction for fcc aluminium using the embedding scheme described in subsection IV A. Embedded atoms are at 0.00 and 7.01 Å. The dashed line shows the Kohn-Sham result and the solid line the embedding results for a) $T_{TF-\frac{1}{2}W}$ functional, b) $T_{PW86}$ functional and c) $T_{nloc}$ functional (see text).](image-url)
At first representing the electron density as the sum of two Kohn-Sham representations may seem like a waste of computational effort since the evaluation of the approximate kinetic energy functional for the entire system does not require anything more than the electron density itself. However, it could be useful in two different ways.

First it allows non-local pseudopotentials to be applied directly to each part of the system within the Kohn-Sham framework (see subsection IV C). Second the results will tell us whether the error in \( T^{n\text{add}}[\rho_1, \rho_2] \) is greater or smaller than the error in \( T^{n\text{pp}}[\rho_1 + \rho_2] \). This second point is important since for the method described in the previous section to be useful the error in the non-additive kinetic energy must be smaller than the error in the total kinetic energy, as described by the approximate functionals. Some cancellation of errors must take place in \( T^{n\text{add}}[\rho_1, \rho_2] \), and its functional derivative, for this to be the case. From the previous subsection it is apparent that cancellation occurs only to a limited degree, and a similar conclusion has been reached when addressing the accuracy of kinetic energy functionals when used to evaluate interaction energies, both for gradient expansions \( [28] \) and semi-local enhancement factor approximations \( [27] \).

In order to obtain the required functional the non-additive kinetic energy is defined as

\[
T^{n\text{add}}[\rho_1, \rho_2] = T^{n\text{pp}}[\rho_1 + \rho_2] - T_s[\rho_1] - T_s[\rho_2],
\]

(23)

where the first term on the RHS is an approximate functional, and the remaining terms are exact. In the previous subsection all of the functionals in this expression were evaluated using approximate functionals. Equation \( [2] \) is applied as before, with \( T_s[\rho_1] \) and \( T_s[\rho_2] \) exact, but with \( T^{n\text{add}} \) given by Eq. (23). The functional derivative of the non-additive kinetic energy becomes

\[
\frac{\delta T^{n\text{add}}[\rho_1, \rho_2]}{\delta \rho_1} = \frac{\delta T^{n\text{pp}}[\rho_1 + \rho_2]}{\delta \rho_1} - \frac{\delta T_s[\rho_1]}{\delta \rho_1},
\]

(24)

where the first term on the RHS is approximate, and the second exact. To obtain the second term in Eq. (24) the method of Bartolotti and Acharya \( [19] \) is applied. They derive an expression for the functional derivative by replacing the self-consistent potential within the Kohn-Sham equations with the self-consistent potential in terms of the associated Euler-Lagrange equation,

\[
-\nabla^2 \psi_n(k) + \left( \mu' - \frac{\delta T_s[\rho_1]}{\delta \rho_1} \right) \psi_n(k) = \epsilon_n(k) \psi_n(k)
\]

(25)

which gives

\[
\frac{\delta T_s[\rho_1]}{\delta \rho_1} = -\frac{\nabla^2 \psi_n(k)}{\psi_n(k)} - \epsilon_n(k) + \mu'
\]

(26)

where \( \mu' \) is the associated Fermi energy. It should be noted that the Euler-Lagrange equation can be used directly to obtain the functional derivative in terms of the trial potential, but this was found to cause convergence difficulties. To determine \( \mu' \) we use

\[
T_s[\rho_1] = \int \rho_1(r) \frac{\delta T_s[\rho_1]}{\delta \rho_1} d^3r,
\]

(27)

as derived by Liu and Parr \( [50] \).

In effect this second approach corresponds to minimising the energy functional of the entire system with the kinetic energy represented by the approximate kinetic energy functional, but with the additional constraint of \( \rho(r) \geq \rho_2(r) \). Calculations were carried out within this scheme, with all parameters equivalent to those in the previous subsection. Table III shows the total energy per atom, and the associated errors. Generally, the errors in the energy for the semi-local functionals are considerably worse than in Table II as demonstrated by the results for \( T_{PW86} \), but the error for \( T_{TF-\frac{1}{2}vb} \) is similar to the first method. The non-local functional gives by far the most accurate results, with the energy accurate to better than 0.1 eV. Fig. 2a, Fig. 2b and Fig. 2c show the electron density resulting from these calculations, for \( T_{TF-\frac{1}{2}vb} \), \( T_{PW86} \) and \( T^{n\text{loc}} \) respectively. It is immediately apparent that the non-local functional provides a far more accurate electron density than either of the semi-local functionals, and a more accurate electron density than the approach described in subsection IV A.

In subsection IV A errors in the total energy functional are introduced by the non-additive part of the kinetic energy, whereas in this section the errors are due to the approximate total kinetic energy. Bearing this in mind our results indicate that, for the non-local functional, \( T[\rho_1 + \rho_2] \) is particularly well described by \( T^{n\text{loc}}[\frac{1}{2}] \), but \( T[\rho_1] \) and \( T[\rho_2] \) are not quite as accurate (these terms only appear in the non-additive kinetic energy). This difference in the accuracy of the same functional applied to different electron densities can be ascribed to the different characters of the electron densities. Fig. 3 shows embedded, substrate and total electron densities resulting from a calculation of the type described in this section, carried out with the non-local functional. Electron densities are shown along a line in the [110] direction between two embedded atoms on opposite corners of one face of the cubic unit cell (this line is chosen as it includes a substrate atom along its path). It is apparent

| Functional | \( E/eV \) | \( \Delta E/eV \) | \( R/\% \times 10^{-3} \text{Å}^{-3} \) |
|------------|-----------|----------------|----------------|
| \( T^{TF-\frac{1}{2}vb} \) | –58.769 | –0.440 | 3.922 | 25.050 |
| \( T_{PW86} \) | –59.680 | –1.351 | 7.260 | 57.064 |
| \( T^{n\text{loc}}[\frac{1}{2}] \) | –58.411 | –0.082 | 1.204 | 9.180 |

Kohn Sham | –58.329 | – | – | – |
FIG. 2: Electron density in [111] direction for fcc aluminium using the embedding scheme described in subsection IV B. Embedded atoms are at 0.00 and 7.01 Å. The dashed line shows the Kohn-Sham result and the solid line the embedding results for a) $T_{TF-\frac{4}{9}vW}$ functional, b) $T_{PW86}$ functional and c) $T_{nloc}$ functional (see text).

that $\rho_1$ is far from homogeneous, and falls close to zero near the sites of substrate atoms. This is expected to be accompanied by worse performance of $T_{nloc}[\rho_1]$ than $T_{nloc}[\rho_1 + \rho_2]$, since this approximate functional is derived using arguments based on the linear response of a homogenous electron gas. It has previously been found that this functional is particularly successful for the total electron density of bulk aluminium with the pseudopotential applied here [6]. Similar considerations lead us to conclude that in general for semi-local functionals the difference $T_{app}[\rho_1 + \rho_2] - T_{app}[\rho_1] - T_{app}[\rho_2]$ is more accurate than $T_{app}[\rho_1 + \rho_2]$ (or about the same accuracy for the particular form $T_{TF-\frac{4}{9}vW}$).

It is worth noting that the results obtained here for Aluminium show closer agreement with Kohn-Sham results than those obtained by Wang et al [6] using a slightly generalised form of the non-local functional, the same pseudopotential and direct minimisation of the total energy functional. This is probably due to the additional constraint of $\rho(r) \geq \rho_2(r)$ present in the calculation performed here preventing an over-relaxation of the electron density. This constraint can be relaxed by swapping the substrate and embedded systems after self-consistency has been reached, reaching self consistency again and repeating this until convergence of the total system is reached. Performing this ‘Freeze and Thaw’ [22, 25] procedure offers no particular advantage for the test system investigated in this paper and when implemented did not influence any of the conclusions given. The only significant consequence of performing a ‘Freeze and Thaw’ calculation was a ‘drift’ of the electron densities away from their associated atoms. For the non-local and $T_{TF-\frac{4}{9}vW}$ functionals the two electron densities remain localised on their host atoms, whereas for the $T_{PW86}$ (and other enhancement factor functionals) the two electron densities evolved to fill the entire unit cell with no association with the host atoms of region I or II apparent.

C. Non-local pseudopotentials

In past applications of the Hohenberg-Kohn theorem directly to the minimisation of the total energy functional the main problem addressed has been the inaccuracy of the available approximate kinetic energy functionals. An additional problem is how to make use of non-local pseudopotentials when no Kohn-Sham representation of the electron density is available. This problem arises due to the Hohenberg-Kohn theorem being strictly applicable only for a local external potential [51, 52].

For the embedding method applied here no Kohn-Sham representation of the total electron density is available, so it is not immediately apparent how a non-local pseudopotential can be applied. This issue has been addressed previously, for example Shah et al [9] provide an ad hoc prescription, by taking the square root of the
and generalise it to the approximation where we take the exact expression around the site of the embedded atoms. Bearing this in mind we take advantage of the fact that the electron density potential energy is given by implicit in the normal application of non-local pseudopotential. Here we make two assumptions. First, that the Kohn-Sham density matrix \( \gamma_s(\mathbf{r}, \mathbf{r}') \), given by

\[
\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_i w_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}'),
\]

(28)

(where \( w_i \) is the occupation number for state \( i \)) is an accurate enough representation of the actual many-body 1st order reduced density matrix (this is the assumption implicit in the normal application of non-local pseudopotentials within the standard Kohn-Sham scheme). Assuming this to be a valid approximation the external potential energy is given by

\[
E_{ext}[\gamma_s(\mathbf{r}, \mathbf{r}')] = \int v(\mathbf{r}', \mathbf{r})\gamma_s(\mathbf{r}, \mathbf{r}')d^3\mathbf{r}'d^3\mathbf{r}
\]

(29)

where \( v(\mathbf{r}', \mathbf{r}) \) is an external non-local potential. Second we take advantage of the fact that the electron density component \( \rho_2(\mathbf{r}) \) is mostly localised near the atomic sites in the substrate, and \( \rho_1(\mathbf{r}) \) is expected to remain localised around the site of the embedded atoms. Bearing this in mind we take the exact expression

\[
\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})
\]

(30)

and generalise it to the approximation

\[
\gamma_s(\mathbf{r}, \mathbf{r}') \approx \gamma_{s,1}(\mathbf{r}, \mathbf{r}') + \gamma_{s,2}(\mathbf{r}, \mathbf{r}'),
\]

(31)

where \( \gamma_{s,1} \) and \( \gamma_{s,2} \) are the 1st order reduced Kohn-Sham density matrices corresponding to electron densities \( \rho_1(\mathbf{r}) \) and \( \rho_2(\mathbf{r}) \). Of course this can only be exact, over all space, if there is no overlap between the electron densities, as can easily be deduced from the fact that there is a non-additive component to the kinetic energy functional in the first place.

Approximation (31) immediately leads to

\[
E_{ext}[\gamma_s] \approx \int V_{loc}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + V_{nloc}[\gamma_{s,1}] + V_{nloc}[\gamma_{s,2}]
\]

(32)

where the first term is the local part of the potential, and the second and third terms are the contributions of the embedded and substrate systems due to the non-local part of the pseudopotentials of all the atoms. Conventional norm-conserving pseudopotentials are non-local only between points on the surface of spheres centred on each atomic site, and only for spheres with a radius less than a certain value, \( r_c \). This implies that the approximation in Eq. (31) need only be accurate between points on each such sphere. Since \( \rho_2(\mathbf{r}) \) is largely localised near the atomic sites in the substrate, and \( \rho_1(\mathbf{r}) \) is expected to remain localised near the embedded atomic sites, Eq. (32) provides a reasonable approximation.

Calculations were carried out for fcc Al with all parameters as before, and using the approach given in subsection IV A but with a Kerker non-local pseudopotential. Fig. 4 and Table III show results for a calculation with \( \rho_2(\mathbf{r}) \) frozen and for the \( T_{TF-\frac{1}{2}vW} \), \( T_{PW86} \) and non-local functionals. These results should be compared with those of Fig. 1 and Table I. For the total energies both \( T_{TF-\frac{1}{2}vW} \) and \( T_{nloc} \) yield results essentially as accurate as those obtained for the local pseudopotential in subsection IV A while \( T_{PW86} \) is less accurate. Fig. 4 shows a higher peak error in the electron densities, but it is difficult to attribute this to a particular aspect of the approximations inherent in the implementation of the non-local pseudopotential. We conclude that a non-local pseudopotential can be used within this method with no significant loss of accuracy.

| Functional | \( E/eV \) | \( \Delta E/eV \) | \( R/\% \) | \( \times 10^{-3} \AA^{-3} \) |
|------------|------------|----------------|----------|-----------------|
| \( T_{TF-\frac{1}{2}vW} \) | 57.148 | 0.120 | 4.349 | 25.267 |
| \( T_{PW86} \) | 56.262 | 0.767 | 7.137 | 41.953 |
| \( T_{nloc} \) | 56.940 | 0.088 | 6.343 | 43.735 |
| Kohn Sham | 57.028 | — | — | — |

TABLE III: Total energy per atom \( E \), and errors in energy \( \Delta E \) and electron density. Results obtained with embedding scheme described in subsection IV A using a non-local pseudopotential.
FIG. 4: Electron density in [111] direction for fcc aluminium using the embedding scheme described in subsection IV A and a non-local pseudopotential. Embedded atoms are at 0.00 and 7.01 Å. The dashed line shows the Kohn-Sham result and the solid line the embedding results for a) $T_{TF-4+}W$ functional, b) $T_{PW86}$ functional and c) $T_{nloc}^{\perp}$ functional (see text).

V. DISCUSSION AND CONCLUSION

We have implemented the partially frozen electron density approach of Cortona [21] and Wesolowski and Warshel [22, 23] using a plane-wave basis, both local and non-local pseudopotentials, and for a metallic system. Although some numerical instabilities are introduced by using a plane-wave representation these are controlled using methods previously developed for exchange-correlation energies and potentials. Several approximations for the kinetic energy functional are considered, including the semi-local enhancement factor approximations that have previously been applied within this method. In addition a modified Thomas-Fermi/von Weizsacker functional and a non-local functional are implemented.

A lattice of aluminium atoms is embedded into a substrate lattice of atoms to create bulk fcc aluminium, and we find that the semi-local functionals result in total energies within $\sim 0.2 - 0.5$ eV per atom of the Kohn-Sham result, and the non-local functional results in an energy differing by $\leq 0.1$ eV per atom. Kohn-Sham electron densities are reproduced reasonably closely. The non-local functional performs best with a peak error of $\sim 20$ milli-electrons Å$^{-3}$ while the semi-local functionals result in errors of $\sim 30$ milli-electrons Å$^{-3}$. Calculations performed with a non-local pseudopotential produce results for the total energy and electron density which are of comparable accuracy to the local pseudopotential case.

Calculations are also carried out for an altered form of the method where part of the kinetic contribution to the embedding potential and energy is obtained exactly. This corresponded to performing a Hohenberg-Kohn minimisation of the total energy expressed in terms of the electron density with an approximate kinetic energy functional applied to the entire system. As implemented here this minimisation allows the use of non-local pseudopotentials, and introduces the constraint $\rho \geq \rho_2$ where $\rho_2$ is some reference substrate system. Results are worse than for the true embedding scheme for all the semi-local functionals, with the exception of $T_{TF-4+}W$ which gives a slightly greater error in the energy, but a slightly improved electron density. From this it seems reasonable to conclude that the approximate non-additive kinetic energy is more accurate than the approximate total kinetic energy for these functionals. The non-local functional gives the most accurate results, with the energy accurate to $< 0.1$ eV atom$^{-1}$ and the electron density accurate to $< 10$ milli-electrons Å$^{-3}$. This suggests that the non-local functional produces the most accurate representation of the both the value of the kinetic energy functional and its functional derivative, and that the errors in the functional derivative are greatest when the electron density is low.

We interpret the extremely good agreement between the Kohn-Sham electron density and embedding results found in subsection IV B (see Fig. 2c) in comparison with that found in subsection IV A (Fig. 1c) for the non-local
functional to be due to the success of this functional in describing bulk aluminium as discussed by Wang et al. For systems where the total electron density is far from homogeneous (e.g., surface/adsorbate) this success of the method of subsection III.B is not expected to hold. In future applications the non-local functional and the method of subsection IV.B are expected to provide the most accurate reconstruction of the full Kohn-Sham result.

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