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Electronic Structure Calculations Using Self-Adaptive Multiscale Voronoi Basis Functions

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The multiscale self-adaptivity of Voronoi basis functions is currently proving to be useful for the simulation of complex fluid systems involving structures on a number of distinct lengthscales. In this paper, we explore the possibility of extending the use of such multiscale basis functions to the framework of density functional theoretic electronic structure computations.

KEY WORDS: Electronic structure theory; multiscale modelling; self-adaptive mesh.

1. INTRODUCTION

Electronic structure calculations based on density functional theory (DFT) and the Kohn–Sham (KS) equations$^{(1)}$ have enjoyed great success in a wide range of applications over recent years.$^{(2–4)}$ Several different techniques have been developed to reduce the high computational cost of such simulations. They can be classified as standard matrix diagonalisations, steepest descent methods and dynamic minimization techniques such as the Car–Parrinello method.$^{(5, 6)}$

All of these methods make use of plane waves (PW) to expand the KS orbitals. Plane waves have several advantages when computing the different terms of the KS effective potentials. First, plane waves are independent of atomic-position, so that the forces acting on the ions are simple to

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handle; using fast-Fourier transform (FFT) techniques, it is straightforward to compute convolution integrals while integrals over the wave functions (scalar products) reduce to simple multiplications of the expansion coefficients. However, there are disadvantages as well in using plane waves, because a very large number of them are needed to resolve the rapid variations of the electron density around the nuclei. In a PW expansion it is quite hard to increase the resolution locally and the computational resources are deployed inefficiently.

Several modifications of the algorithms have been proposed recently, with the aim of increasing the resolution of the expansion of the orbitals only in local regions around the positively charged nuclei, primarily using Gaussian basis functions together with standard PWs to enlarge the expansion basis. However, some rather more sophisticated techniques have also been advocated, including a number of real-space finite-difference, finite-element and adaptive mesh methods (see, for example, the interesting papers by Gygi(7, 8) and the review by Beck(9)) and the divide-and-conquer approach based on localised basis functions by Yang.(10) Some of these multiscale solvers are computationally competitive with the most efficient plane wave methods, while conferring various additional algorithmic benefits owing to their local features.

A similar need for multiscale algorithms is encountered in an at first sight far removed field of research, namely the modelling and simulation of non-Newtonian dense colloidal suspensions, part of the modern science of soft condensed matter. In this case, the Navier–Stokes equations are used to describe the single component Newtonian solvent surrounding the colloidal particles; the discrete grid must be able to resolve the fluid length scales around the colloidal particles with much better accuracy than far away from them to ensure proper representation of hydrodynamic and lubrication interactions. The need for consistent multiscale methods is exacerbated in more complex fluid systems, for example ones in which there may be colloids and polymers, and *a fortiori* for such multicomponent fluids flowing in porous media, a common real world situation. The problem we encounter in complex fluid systems of large spatial scale separation between the background scale and the colloidal particles is quite reminiscent of the situation in electronic structure calculations, where one encounters a similar scale separation between the electronic fluid and the heavy nuclei. Any simulation technique must be able to bridge several orders of magnitude in length scales to reliably handle such calculations. Brute force is always one route, but it rapidly becomes computationally overwhelming.

For the case of complex fluids a multiscale "dissipative particle dynamics" technique based on the Voronoi tessellation(11, 12) has been recently been introduced.(13–15) Here a Lagrangian scheme based on an adaptive Voronoi tessellation is used to resolve space length-scales non-uniformly.

The aim of the present paper is to draw parallels between electronic structure calculations and complex colloidal fluids, in the belief that some knowledge from complex fluid dynamics can be exported to the quantum many-body framework. In this picture, the KS orbitals become an electronic multi-component fluid composed of many separate single electron fluids which interact via the KS potential.

In such an electronic fluid, the ions composed of the nuclei and the core electrons can be interpreted as “colloidal particles” interacting, through the Hellmann–Feynman electronic force, with the multi-component electronic fluid, with the appropriate pseudo-potentials for nucleus plus core electrons. The advantage of this “fluid form” expansion of the wave function is that the discretisation is *self-adaptive* and may even provide an optimal representation of electronic orbitals.

2. DENSITY FUNCTIONAL THEORY

The Kohn–Sham (KS) equations allow the reduction of the dimensionality of the general wave function Ψ on a phase space of dimensionality $3N$ to N wave functions Ψ_i in three dimensions coupled by an effective potential $V^{\text{eff}}(\mathbf{r}) = V^{\text{ext}}(\mathbf{r}) + V^{HT}[n(\mathbf{r})] + V^{xc}[n(\mathbf{r})]$, given in terms of the external potential V^{ext}, the Hartree potential $V^{HT}(\mathbf{r}) = \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ and the exchange V^{xc} potential, which are functionally dependent on the electron density $n(\mathbf{r})$.(1) These equations have the following form:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{\delta V^{\text{eff}}}{\delta n(\mathbf{r})} \right\} \Psi_i = \varepsilon_i \Psi_i \tag{1}$$

The computation of the ground electronic state requires several diagonalisation calculations until the variation of the energy with respect to the total electronic density is zero. If the ion dynamics is added, then for each functional minimization, the ions are moved and the ground state computed again. The forces due to the electronic degrees of freedom are calculated using the Hellmann–Feynman theorem:

$$F_I = -\frac{\partial E}{\partial R_I} = \langle \Psi | \frac{\partial H}{\partial R_I} | \Psi \rangle \tag{2}$$

where R_I is the position of the Ith ions comprising the nucleus and core electrons of the chosen atom.

Another possibility to obtain the ground state is to use the Schrödinger equation in imaginary time

$$\hbar\dot{\Psi}_i = -H\Psi_i \tag{3}$$

where the dot indicates the total derivative. Due to the quicker exponential decay of the higher energy states, the long time solution isolates the ground state while the excited states are filtered out. This method is formally equivalent to steepest descent (SD) minimisation with $\frac{\delta E}{\delta \Psi_i^*(\mathbf{r},t)} = 2H\Psi_i$. The solution of the imaginary time Schrödinger equation gives a decaying dynamics which is different from the solution of the real time Schrödinger equation describing all the excited states.

A further technique for electronic structure minimisation is the Car–Parrinello (CP)$^{(5)}$ method which eliminates the need for eigenvalue calculations and replaces Eq. (1) with a fictitious Newtonian dynamics which is equivalent to the KS equations (1) close to convergence and where the ion dynamics is considered at the same time as electronic energy minimisation.

Each of these methods requires a series expansion of the single particle wave functions. As discussed above, often a plane wave expansion is used. However, when the electrons are highly localised, the plane wave expansion engenders severe memory requirements on the computational hardware. Alternative approaches have been proposed over the years. One possible solution is to use Gaussian walkers to approximate the electronic wave function, an approach which meets with a problem of ill-posedness if two or more Gaussians overlap. This is equivalent to using a basis with parallel and therefore degenerate functions. Certain other methods use a hybrid system in which the total density is expanded in both plane waves and Gaussian walkers so as to simplify the calculation of the effective potential.$^{(16)}$

Given N atoms and M basis functions, to expand the orbitals the KS method is computationally $O(NM^3)$, with $O(M^3)$ being the time for the diagonalisation of Eq. (1) for any orbital; the SD method requires $O(NM^2)$ to compute the action of the Hamiltonian on the wave-functions and $O(N^2M)$ for the orthonormalisation, but can be optimised in $O(NM + N^2M + NM\log(M))$, so that the term $O(N^2M)$ dominates; the CP method has computational cost $O(N^3)$ due to the delocalised nature of plane wave expansions, reorthogonalisation of the orbitals being computationally very expensive.$^{(6)}$

3. QUANTUM WAVE PACKETS

The hydrodynamic formulation of a quantum system is obtained by simply rewriting the general wave function in the eikonal form

$\Psi(\mathbf{r}, t) = R(\mathbf{r}, t)\, e^{iS(\mathbf{r}, t)/\hbar}$ with R and S real valued functions. By inserting this in the time dependent Schrödinger equation and separating real and imaginary parts, we find

$$\hbar \frac{\partial R}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{2}{\hbar} \nabla R \cdot \nabla S + \frac{1}{\hbar} R \nabla^2 S \right) \tag{4}$$

$$-R \frac{\partial S}{\partial t} = -\frac{\hbar^2}{2m} \left(\nabla^2 R - \frac{1}{\hbar^2} R (\nabla S)^2 \right) + VR \tag{5}$$

Multiplying both sides of (4) by R and both sides of (5) by ∇ and using the notation $\rho(\mathbf{r}, t) = R(\mathbf{r}, t)^2$ and $\mathbf{v}(\mathbf{r}, t) = \nabla S(\mathbf{r}, t)/m$, we have that

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \rho = \frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v} \tag{6}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{v} = \frac{d\mathbf{v}}{dt} = -\nabla (Q + V) \tag{7}$$

where $Q[\rho] = -\frac{\hbar^2}{2m} \frac{1}{R} \nabla^2 R = -\frac{\hbar^2}{2m} \rho^{-1/2} \nabla^2 \rho^{1/2} = -\frac{\hbar^2}{4m} \left(\frac{\nabla^2 \rho}{\rho} - \frac{1}{2} \frac{(\nabla \rho)^2}{\rho^2} \right)$. The time dependent quantum potential Q is a special feature of the quantum system and vanishes in the limit $\hbar \to 0$, when the dynamics reduces to classical dynamics governed by the classical potential V. Equations (6) and (7) correspond to an ideal (dissipationless) compressible fluid, and are therefore amenable to the wide arsenal of numerical methods for studying fluid flow. In particular, we shall consider so-called "Lagrangian" techniques, based on a particle representation.(17)

The density $\rho(\mathbf{r}, t)$ and velocity $\mathbf{v}(\mathbf{r}, t)$ fields representing the initial state of the wave function Ψ are approximated by M point particles with associated trajectory $\mathbf{r}_k(t)$, mass m, velocity $\mathbf{v}_k(t) = \mathbf{v}(\mathbf{r}_k, t)$ and density $\rho_k(t) = \rho(\mathbf{r}_k, t)$, $k = 1, \dots, M$. The time evolution is governed by Eqs. (6) and (7) and the kinematic condition

$$\frac{d\mathbf{r}}{dt} = \mathbf{v} \tag{8}$$

The gradient and further derivatives of the density $\rho(\mathbf{r}, t)$ and velocity $\mathbf{v}(\mathbf{r}, t)$ fields are computed via a dynamic local interpolation over the point particles k.(18) At any time, the quantity $|\Psi(\mathbf{r}, t)|^2$ can be computed via the point-like information ρ_k, $k = 1, \dots, M$.

The Lagrangian fluid formalism is ideally suited to adaptive mesh methods of solution, but it does not allow a straightforward calculation of integrals involving the orbitals. In fact, to do this one would have to reconstruct the phase S from the gradient of the phase. To avoid this extra work, we evolve the phases instead of the velocity $\mathbf{v}$ itself:

$$\frac{\partial S}{\partial t} = -(Q+V) + \frac{1}{2m}(\nabla S)^2 \tag{9}$$

$$\mathbf{v} = \frac{\nabla S}{m} \tag{10}$$

The quantum wave packet Eqs. (6), (7) are derived directly from the real time Schrödinger equation; therefore they give the time dependent dynamics of the wave function. In order to obtain the ground state we must add a friction term $-\eta\mathbf{v}$ to the velocity equation (7).$^{(19)}$ Doing that, the time derivative of the gradient of the wave function is zero and the phase stationary. For the phase evolution the same friction term reads $-\eta S$.

4. THE QUANTUM MECHANICAL EQUATIONS IN FLUID FORM

In this section we shall make use of the aforementioend analogy between electronic and colloidal fluids to recast the Kohn–Sham equations in fluid form. We wish to emphasize that, being based on the Kohn–Sham equations, our formalism shares the standard limitations inherent with the Born–Oppenheimer approximation, that is a clearcut scale separation between electronic and nuclear degrees of freedom. As a result it cannot be expected to describe non-adiabatic events associated with crossing of energy levels, such as cluster-cluster scattering.

The fluid form of the KS equations for N atoms with trajectories $\mathbf{R}_I(t)$, $i = 1,\ldots, N_{occ}$, single-particle orbitals $\Psi^{(i)}(\mathbf{r}, t)$, and $k = 1,\ldots, M$ point particles, for any electronic orbital can be discretised on a Lagrangian finite volume Voronoi tessellation.$^{(13–15)}$ Given a set of points $\{\mathbf{r}_1,\ldots, \mathbf{r}_M\}$, a partition of the space assigning every point to its nearest site is called a Voronoi tessellation. We can define the characteristic function for the partition $k^{(15)}$ $H^t_k(\mathbf{r}) = \prod_{l=1}^{M} H((\mathbf{x} - \frac{\mathbf{r}_k(t)+\mathbf{r}_l(t)}{2})\cdot \mathbf{e}_{kl})$ where H is the one-dimensional Heaviside function with derivative $\delta(x)$ and $\mathbf{e}_{kl} = \frac{\mathbf{r}_k - \mathbf{r}_l}{|r_k - r_l|}$. Using the characteristic function of the Voronoi tessellation $H^t_k(\mathbf{r})$ we can coarse-grain the electronic fluids in the same manner as is done in complex fluid is by defining

$$\rho^{(i)}_k(t) = \frac{1}{V_k}\int \rho^{(i)}(\mathbf{r}, t)\, H^t_k(\mathbf{r})\, d\mathbf{r} \tag{11}$$

$$\mathbf{U}^{(i)}_k(t) = \frac{1}{V_k}\int \mathbf{v}^{(i)}(\mathbf{r}, t)\, H^t_k(\mathbf{r})\, d\mathbf{r} \tag{12}$$

$$S^{(i)}_k(t) = \frac{1}{V_k}\int S^{(i)}(\mathbf{r}, t)\, H^t_k(\mathbf{r})\, d\mathbf{r} \tag{13}$$

where V_k is the volume of the partition k. The Lagrangian dynamics of the tessellation is reflected by the time dependence of the characteristic function. The Voronoi centers $\mathbf{r}_k$ move according to the kinematic condition $\dot{r}_k = \mathbf{U}_k$ where $\mathbf{U}_k = \frac{1}{M}\sum_i \mathbf{U}_k^{(i)}$ is the average velocity of the total electron cloud in the volume k.

Writing the time derivatives as $\dot{\rho}_k^{(i)}$, $\dot{\mathbf{U}}_k^{(i)}$ we can obtain the temporal evolution of the system. For the time dependence of the density we have that

$$\dot{\rho}_k^{(i)} = \frac{1}{V_k}\left[-\dot{V}_k\rho_k^{(i)} + \int (\partial_t \rho^{(i)} H_k^t + \rho^{(i)}\dot{H}_k^t)\, d\mathbf{r} \right] \tag{14}$$

The first term together with the second integrand on the right hand side of this equation arise due to volume variations, which are intrinsic to the method and have previously been derived explicitly in the complex fluid case without any particular difficulties.$^{(15)}$ The first term $\dot{V}_k$ can be computed as

$$\dot{V}_k = \sum_l \dot{V}_{kl} \tag{15}$$

$$\dot{V}_{kl} = -\frac{\mathbf{U}_k + \mathbf{U}_l}{2} \cdot \mathbf{e}_{kl} l_{kl} + l_{kl}\mathbf{L}_{kl} \cdot \dot{e}_{kl} \tag{16}$$

where l are the neighbouring volumes, l_{kl} is the surface area between k and l, $\mathbf{L}_{kl} = (\mathbf{l}_{CM} - \frac{\mathbf{r}_k - \mathbf{r}_l}{2})$ and $\mathbf{l}_{CM}$ is the position of the centre of mass of the surface between k and l. The third term yields

$$\int \rho^{(i)}\dot{H}_k^t\, d\mathbf{r} = \sum_l \langle \rho^{(i)} \rangle_{kl}\, \dot{V}_{kl} \tag{17}$$

where $\langle \cdot \rangle_{kl}$ is the average on the surface kl. The average can be taken by using a linear interpolation as $\langle \rho^{(i)} \rangle_{kl} = \frac{1}{2}(\rho_k^{(i)} + \rho_l^{(i)})$.

The second term in Eq. (13) depends on Eq. (6) and is transformed using Gauss's theorem on the volume k as

$$\frac{1}{V_k}\int \partial_t \rho^{(i)} H_k^t\, d\mathbf{r} = \frac{1}{V_k}\sum_l l_{kl} \langle \rho^{(i)}\mathbf{v}^{(i)} \rangle_{kl} \cdot \mathbf{e}_{kl}; \tag{18}$$

$\mathbf{e}_{kl}$ (defined before) is normal to that surface (a Voronoi property). The velocity equation follows the same derivation as for the density, and we therefore omit it here.

The final set of differential equations for the electronic fluid is given by

$$\frac{d\mathbf{r}_k}{dt} = \mathbf{U}_k \tag{19}$$

$$\frac{d\rho_k^{(i)}}{dt} = \frac{1}{V_k}\sum_l \left[l_{kl}\, \frac{\rho_k^{(i)}\mathbf{v}_k^{(i)} + \rho_l^{(i)}\mathbf{v}_l^{(i)}}{2}\cdot \mathbf{e}_{kl} + \frac{\rho_l^{(i)} - \rho_k^{(i)}}{2}\dot{V}_{kl} \right] \tag{20}$$

$$\begin{aligned}\frac{dS_k^{(i)}}{dt} = {} & -Q_k[\rho^{(i)}(\mathbf{r}, t)] - V^{\text{eff}} + \frac{1}{2}m(U_k^{(i)}) \\ & -\eta S_k^{(i)}(\mathbf{r}, t) + \frac{1}{V_k}\sum_l \frac{S_l^{(i)} - S_k^{(i)}}{2}\dot{V}_k\end{aligned} \tag{21}$$

$$\mathbf{U}_k^{(i)} = -\sum_l l_{kl}\mathbf{e}_{kl}S_l^{(i)} \tag{22}$$

$$\frac{d^2\mathbf{R}_I}{dt^2} = \frac{\mathbf{F}_I}{M_I} \tag{23}$$

$$k = 1,\ldots, M; \quad I = 1,\ldots, N; \quad i = 1,\ldots, N_{occ}$$

where Q_k and V_k^{eff} are the interpolations of the quantum potential Q and effective potential $V^{\text{eff}}(\mathbf{r}) = V^{\text{ext}}(\mathbf{r}) + V^{HT}[n(\mathbf{r})] + V^{xc}[n(\mathbf{r})] + \text{constraints}$, $\mathbf{F}_I$ is the Hellmann–Feynman force (2) due to the electronic structure of the ions, and

$$n(\mathbf{r}, t) = \sum_i^{N_{occ}} |\Psi^{(i)}|^2 = \sum_i^{N_{occ}} \rho^{(i)}(\mathbf{r}, t) \tag{24}$$

is the total density of the electron clouds. The quantum potential is

$$Q[\rho^{(i)}] = -\frac{\hbar^2}{4m}\left(\frac{\nabla^2\rho^{(i)}}{\rho^{(i)}} - \frac{1}{2}\frac{(\nabla\rho^{(i)})^2}{(\rho^{(i)})^2}\right) \tag{25}$$

The non-local Hartree–Fock potential

$$V^{HF}[n(\mathbf{r})] = \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \tag{26}$$

is computed through the FFT algorithm as a convolution product when the wave function is expanded in plane waves. The potential V^{xc} depends on the exchange and correlation energy approximations used, which is local in the LDA (local density approximation). In this case it does not introduce any particular algorithmic problem. The V^{ext} potential is the total external potential felt by the electrons due to nuclei plus core electrons, which are represented as pseudo-ions with particular pseudo-potentials.

During the dynamics the orbitals must remain orthonormal at all times. This requirement must be imposed at any time step by reorthogonalisation of the orbitals with any orthonormalisation method, such as the Gram–Schmidt procedure. This is represented by the constraints term in the potential.

Comparing with the discretisation in terms of walkers as given in the previous sections, the Voronoi tessellation gives an additional parameter, the volume. This is a fundamental feature in complex fluid simulations because we want to compute the fluctuations of the fluid; in the present quantum fluid context, the volume is used to compute the scalar products which are space integrals.

We note that the present scheme is directly applicable to time-dependent density-functional calculations by setting the friction coefficient $\eta = 0$, since our equations are intrinsically time-dependent, being based on the time-dependent Kohm–Sham equations.(20)

Before moving to the analysis of the present scheme, it is worth mentioning a possible alternative formulation of the "partition function" $H_k^t(\mathbf{x})$. As previously stated, $H_k^t(\mathbf{x})$ is a characteristic function of the Voronoi cell associated with the point $\mathbf{r}_k$. It is possible to define a smooth characteristic function $f_k^t(\mathbf{x})$, which can be thought as a regularisation of $H_k^t(\mathbf{x})$, as $f_k^t(\mathbf{x}) = \frac{g(\mathbf{x}-\mathbf{r}_k)}{\sum_l g(\mathbf{x}-\mathbf{r}_l)}$, where $g(\mathbf{x}) = \exp(-x^2/a^2)$ and a is a scale length parameter. In the limit $a \rightarrow 0$, f_k^t reduces to H_k^t, while for a finite value a each Voronoi cell shares an overlapping region with all its neighbouring cells.(14) The width of the overlap is dependent on a and on the form of the function g.

This definition of a smooth "partition function" is strongly reminiscent of the "partition function" proposed by Yang(10) in his linear scaling divide-and-conquer method. Having noted the similarity in terms of the choice of the partition function, we point out that the divide-and-conquer scheme localises the wave-function around each atom of the molecular system, and subsequently expands the local wave-function onto a local basis set. In our case, we use the partition function to provide an expansion of the electronic fluids directly, therefore our description is entirely based on the Voronoi tessellation together with the fluid form equations without any further expansion onto other basis sets.

5. SOLVING THE QUANTUM DISSIPATIVE EQUATIONS

The actual solution of Eqs. (19)–(23) presents a number of technical challenges, primarily due to the non-locality of the effective potential and to the orthogonalisation step, i.e., the calculation of scalar products $\int \Psi_i^* \Psi_j \, d\mathbf{r}$.

The first, weak, non-locality is given by the high order derivatives of the quantum potential which require higher order interpolation than that usually performed in classical fluid mechanics. In fact, the quantum fluid form of the equations contains third-order spatial derivatives of the density, while in the Navier–Stokes equations only second order velocity derivatives are involved.

A second, much stronger, non-locality is given by the Hartree potential. This involves a spatial integral of the total electronic density or the equivalent solution of the Poisson problem

$$\nabla^2 V^{HF} = n \tag{27}$$

This is most efficiently handled via the Fast Fourier Transform (FFT). However, since we are working with an unstructured set of particles, direct use of Fourier transforms is ruled out. We can use particle-mesh solvers, in which the Poisson equation is solved on a regular grid (incurring, however, the loss of adaptability of the total density n)(9) or finite element Poisson solvers using the existing Delaunay triangulation provided by the Voronoi tessellation.

The fluid form appears particularly ill-suited to the imposition of orthogonality. The scalar products

$$\int (\rho^{(i)}(\mathbf{r}, t)\, \rho^{(j)}(\mathbf{r}, t))^{1/2}\, e^{iS_{(ij)}(\mathbf{r}, t)/\hbar}\, d\mathbf{r} \tag{28}$$

where the phase $S^{(ij)} = S^{(i)} - S^{(j)}$, must be computed for any pair i, j. However, given that we know the volume for any k, a possible discretisation of the previous integrals is

$$\sum_k (\rho_k^{(i)} \rho_k^{(j)})^{1/2}\, e^{iS_k^{(ij)}/\hbar} V_k \tag{29}$$

where V_k is the volume of the kth Voronoi cell. This Riemann approximation of the integral involves more computational time than the analogue arising for plane waves, due to the need for numerical evaluations of the exponentials.

The orthonormalisation step needed to compute integrals of the previous type do not present any particular problem. For instance, a SHAKE type of algorithm(21) could be written for the constraints on the variables $S_k^{(i)}, \rho_k^{(i)}$ for varying k, i using Eq. (29) as the constraint hyper-surface.

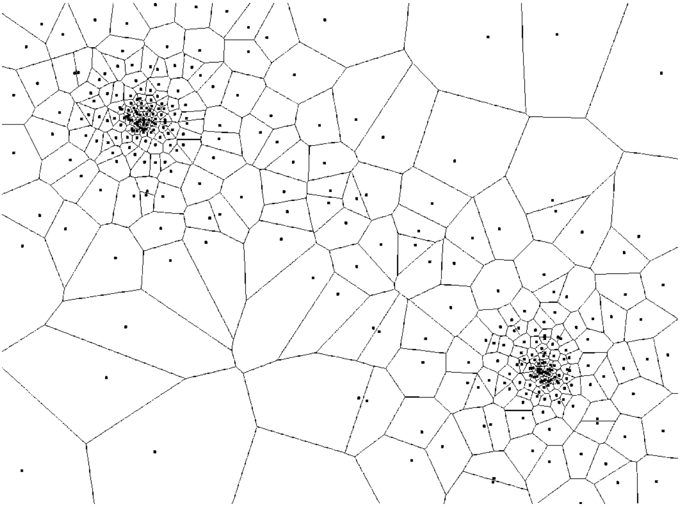

Fig. 1. The adaptability of the Voronoi tessellation is shown in two-dimensions for ease of visualisation. The dense regions correspond to the neighbourhood of the ions while the resolution of the inter-ionic regions is coarser.

The Voronoi tessellation used to coarse-grain all the electronic fluids is less expensive the number of atoms increases, while the Lagrangian structure of the equations becomes progressively worse. In fact all individual single orbitals move according to their own dynamics, while the tessellation is updated with the averages of the electronic fluid velocities. However, if all the electronic density within the orbitals remains concentrated around the ions, it is expected that the tessellation will resolve the right length scales for all the electronic fluids (that is, the electronic orbitals).

Due to high-compressibility, and lack of dissipation, the electronic fluid might develop sharp features (shock fronts) or even topological singularities (vortices) which would eventually spoil the single-valuedness of the phase S. While these effects present a definite challenge to any numerical methods, we believe the present scheme is relatively well positioned to handle them successfully, because our technique is naturally adaptive, so that particles have a built-in tendency to cluster around sharp features of the fluid flow (see Fig. 1).

6. CONCLUSION

In the present paper, we have derived the fluid form of the Kohn–Sham equations for the orbitals of a collection of atoms. The ground state is obtained by adding a friction term to the fluid velocity of the electronic cloud. The orbitals are expanded on a self-adaptive Lagrangian Voronoi tessellation which should naturally cluster around the ions. The common support for all the orbitals of the Voronoi tessellation is used to compute the integrals of the scalar products for the orthonormalisation of the wave functions. The non-local Hartree potential and any other non-local potential can be solved using the structure of the Delaunay triangulation underlying the Voronoi tessellation.

One possible advantage of this technique is to resolve different length scales present in the electronic structure in a uniform and coherent manner. This means a much smaller number M of basis functions than need to be used in standard plane wave expansions, significantly reducing the overall complexity of the problem. Some additional effort would be needed in order to update the Lagrangian tessellation and to implement periodic boundary conditions. However, this somewhat complex machinery is already available for complex fluid simulations(15) and therefore no additional effort is required to implement it for electronic structure studies.

Inevitably, the final word on the viability of the scheme we have proposed here must rest with numerical implementations, which we hope will be carried out in the near future.

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