The planewave pseudopotential method

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In the following, the problem of evaluating quantum mechanically the ground-state electronic density and total energy of a system of interacting electrons for a given nuclear configuration is discussed. While the core of the methodology is presented here, more detailed reviews can be found in Jones and Gunnarsson [16] (on the Density Functional formalism) and in Payne *et al* [24] (on its applications to first principles molecular dynamics).

1.1 The many-body Schrödinger equation

The behaviour of a system of N electrons can be predicted simply by solving the Schrödinger Equation for the system:

$$\hat{H}\Psi = E\Psi \tag{1}$$

The problems arise in attempting to solve this equation. Ψ is the many-body wavefunction and is an anti-symmetric function (to satisfy the Fermi statistics of electrons) of the electron co-ordinates $\{\mathbf{r}_i : i = 1, N\}$, and the Hamiltonian, $\hat{H}$, is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla^2_{\mathbf{r}_i} + V_{ext}(\{\mathbf{r}_i\}) + V_{e-e}(\{\mathbf{r}_i\}) \tag{2}$$

The eigenvalue E is the total energy of the system, essentially determined by the external potential V_{ext} which describes the Coulomb interaction between the electrons and a given configuration of nuclei. The term V_{e-e} gives the electron-electron Coulomb interaction, and it is this term which introduces the coupling between the electronic co-ordinates, and precludes a straightforward separation of the many-body wavefunction which would make the solution of the problem very simple computationally.

1.2 Density Functional Theory

It was noted that the term V_{e-e} in the Schrödinger Equation introduces a coupling between the electronic co-ordinates of the many electrons in the system. This coupling is often referred to as "correlation" — as an electron moves the other electrons feel its Coulomb potential, experience a force and move in response. Hence the motion of the electrons is correlated. Although the physics is straightforward, the mathematics of the problem becomes intractable for all but the simplest systems. A step towards the solution of this problem was made by Hohenberg and Kohn [14]. They introduced the concept of the electronic density $n(\mathbf{r})$ as a basic variable, within the framework of density functional theory (DFT). They showed that the ground-state total energy E could be written as a functional of the ground-state electronic density,

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}. \tag{3}$$

where $F[n(\mathbf{r})]$ is a universal functional, so that it is $V_{ext}(\mathbf{r})$ which uniquely describes any particular physical system. Hohenberg and Kohn also showed that the density which minimised E in Equation 3 is the ground-state density. Unfortunately the functional is not known, and hence DFT is of little use in this form.

A practical scheme for DFT calculations became possible following the work of Kohn and Sham [19]. They chose to write the density in terms of a set of orthonormal functions, one for each of the N electrons in the system.

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \tag{4}$$

$F[n(\mathbf{r})]$ is separated into three terms:

$$F[n(\mathbf{r})] = T_S[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})], \tag{5}$$

where T_S is the kinetic energy term,

$$T_S = \sum_i \frac{\hbar^2}{2m} \int \phi_i^* \nabla^2 \phi_i d^3\mathbf{r}. \tag{6}$$

This is not equal to the true electronic kinetic energy for the system, but it is of similar magnitude and most importantly it can be computed exactly. It is known as the non-interacting kinetic energy. Previous approaches to approximating the functional $F[n(\mathbf{r})]$ (e.g. that of Thomas-Fermi [16]) attempted to approximate the kinetic energy purely in terms of the density. These approaches failed, since the kinetic energy makes up large part of the total energy, and the approximations used did not give an accurate enough value for the kinetic energy. The term E_H in Equation 5 describes the Coulomb energy of the electron density $n(\mathbf{r})$, which is the same as the electron-electron energy in the Hartree approximation:

$$E_H = \frac{1}{2} \int \int \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r} d^3\mathbf{r}'. \tag{7}$$

Thus far the terms in the total energy have been defined to be exact. E_{XC} describes the rest of the contributions to the total energy, making up the difference between $T_S + E_H$ and the true functional F. It is known as the *exchange-correlation* energy, and is the only quantity that is approximated in the Kohn-Sham approach. The most common, and straightforward, approximation to E_{XC} is the local density approximation (LDA). Within the LDA, E_{XC} is written as,

$$E_{XC} = \int \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r}) d^3\mathbf{r}, \tag{8}$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per unit volume of a homogeneous electron gas with a density of n. Monte Carlo total energy calculations have been performed for uniform electron gases at a variety of electron densities, and by subtracting T_S and E_H (which can both be straightforwardly evaluated), ϵ_{xc} can be extracted and parameterised [4, 25]. Given that this parameterisation is based on data for homogeneous charge densities, the LDA might be expected only to be strictly valid for systems in which the charge density is slowly varying, which is clearly not the case in a general covalently bound solid. However, experience has shown the LDA to be a very good approximation for a wide variety of systems in the solid state. This success can be attributed to the fact that the LDA adheres to the sum-rule for the exchange correlation hole[11]. It was the failure to ensure that this sum-rule was satisfied which initially caused many supposed improvements to the LDA to fail. Now generalised gradient approximations (GGA) have been developed which obey the sum rule and provide better descriptions of weak molecular bonds than the LDA [17, 26].

Having set up the formalism of Kohn and Sham, its practical implementation is now examined. Through Equation 4, the functional $E[n]$ has now been expressed in terms of a set of functions $\{\phi_i(\mathbf{r})\}$, thus minimising $E[n]$ with respect to this set, subject to the constraint that they remain orthonormal leads to the set of equations:

$$-\frac{\hbar^2}{2m}\nabla^2\phi_i + V_H\phi_i + V_{ext}\phi_i + V_{xc}\phi_i = \varepsilon_i\phi_i, \tag{9}$$

where,

$$V_H = \frac{\delta E_H}{\delta n(\mathbf{r})}, \tag{10}$$

and,

$$V_{xc} = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}. \tag{11}$$

These equations are known as the Kohn-Sham equations and it can now be recognised what role the set $\{\phi_i(\mathbf{r})\}$ is to play. The Kohn-Sham equations clearly resemble non-interacting single particle Schrödinger equations — the $\{\phi_i\}$ being eigenstates and the Lagrange multiplier ε_i the corresponding eigenvalues. Thus the many-body problem described in Section 1.1 has been mapped to one of a system of non-interacting single particles. These single particle states will be interpreted in Section 2, and will turn out to be the states used in the evaluation of optical and other spectral properties. The potentials V_H and V_{xc} depend on the charge density which, through Equation 4, depends of the Kohn-Sham eigenstates. Hence, the Kohn-Sham equations must be solved self-consistently — the potential and the resulting charge density must be consistent.

1.3 Periodic Boundary Conditions

For many years the electronic structure community focussed primarily on the properties of perfect crystalline solids. This has lead to the use of periodic boundary conditions in many electronic structure methods — as in the case of the total energy pseudopotential method. The use of periodic boundary conditions, through Bloch's Theorem (see below) allow the treatment of the very large number of electrons in a crystal. As solid state physicists have moved to the study of less perfectly ordered systems, periodic boundary conditions — although no longer strictly valid — have not been abandoned. They permit the use of the highly desirable planewaves basis (see Section 1.4) and give the choice as to whether the various terms in Equation 9 should be evaluated in real or reciprocal space[15]. However, to study such problems, aperiodicity must be approximated within the supercell approach.

1.3.1 Bloch's theorem

For a one-electron Hamiltonian — for example that in Equation 9 — if the potential has a lattice periodicity (i.e. $U(\mathbf{r}) = U(\mathbf{r}+\mathbf{R})$ for all $\mathbf{R}$ where $\mathbf{R}$ is a lattice vector), then the eigenstates of the Hamiltonian can be written as:

$$\Psi^n_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u^n_{\mathbf{k}}(\mathbf{r}), \tag{12}$$

where $u^n_{\mathbf{k}}$ is a cell periodic functions such that $u^n_{\mathbf{k}}(\mathbf{r}) = u^n_{\mathbf{k}}(\mathbf{r}+\mathbf{R})$ for all lattice vectors $\mathbf{R}$. This implies that:

$$\Psi^n_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}.\mathbf{R}} \Psi^n_{\mathbf{k}}(\mathbf{r}) \tag{13}$$

On substituting $\Psi^n_{\mathbf{k}}(\mathbf{r})$ into Equation 9 a new set of eigenequations for $u^n_{\mathbf{k}}(\mathbf{r})$ is found, one for each value of the continuous variable $\mathbf{k}$. The problem of solving for an infinite number of electrons has become one of calculating for a finite number of bands at an infinite number of $\mathbf{k}$-points[1]. However, physical properties are expected to be smoothly varying functions of $\mathbf{k}$ and hence many integrals can be well approximated by a finite sampling of $\mathbf{k}$[2, 22, 23, 6, 5].

1.3.2 The supercell approximation

The application of periodic boundary conditions forces periodicity on the system studied. This is significant, since many applications of electronic structure calculations are on systems which do not have full three dimensional translational symmetry — for example the study of defects, impurities or even the interaction of molecules and surfaces. In the supercell approximation, aperiodic systems are approximated by enclosing the region of interest

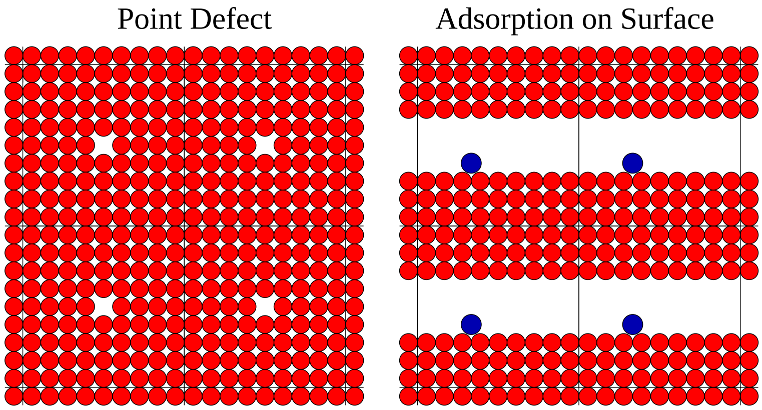

Figure 1: The supercell approximation —the modelling of aperiodicity within periodic boundary conditions.

in either bulk material (for a defect) or vacuum (for a molecule) and then periodically repeating this cell throughout space — see Figure 1. The supercell must be large enough for the fictitious interactions between neighbouring cells to be negligible.

1.4 The planewave basis set

In order to solve the eigenvalue problem of Equation 9 numerically the eigenstates $\{\phi_i\}$ must be represented by some basis set. While there are many possible choices, the one made here is to use planewaves as the basis. There are many advantages in the use of planewaves. They form a mathematically simple basis, giving a very direct representation of the electronic states. Planewave calculations can be taken systematically to convergence as a function of the size of the basis (see below), and when forces are needed for molecular dynamics applications there is no need to consider the Pulay correction forces [27]. This is since the planewaves are not centred about atoms, and so the basis set need not change as the atoms move. However, planewave basis sets require many more basis states per atom than atom-centred orbitals — many hundreds per atom as opposed to of the order of ten. Without the use of pseudopotentials (described in Section 1.5) the use of planewaves would prove impractical in all but the very smallest systems.

The details of the planewave basis are now examined. Application of periodic boundary conditions ensures a discrete (but still infinite) basis set.

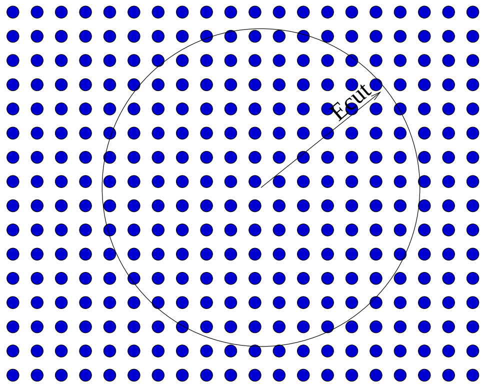

Figure 2: The planewave basis set is defined by the energy cutoff, E_{cut}

The Kohn-Sham eigenstates are expressed as:

$$\Psi_{\mathbf{k}}^{n}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}}^{n}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}}, \tag{14}$$

where the sum is over all reciprocal lattice vectors **G**. To truncate the basis set the sum is limited to a set of reciprocal lattice vectors contained within a sphere with a radius defined by the cutoff energy, E_{cut}:

$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}. \tag{15}$$

Hence, the basis set is defined by the maximum kinetic energy component it contains - see Figure 2. Physical quantities can be converged systematically by increasing E_{cut}.

While, in principle, all basis sets are equally accurate (so long as they are complete) there a many reasons why a particular set might be chosen. There can be a prejudice against the planewave basis — while the lack of a centre for a planewave removes the need to calculate Pulay corrections this lack of a centre can be looked at as a disadvantage. A calculation performed using atom-centred orbitals as a basis (i.e. LCAO) produces wavefunctions with an immediate interpretation in terms of the mixing of those orbitals, the information contained within a wavefunction described in planewaves is less directly accessible. However, work performed by the author (in collaboration with Segall, Shah and Payne) [28, 29] shows that the straightforward planewave representation of wavefunctions allows the same chemical population analyses to be performed as in more traditional quantum chemistry approaches.

1.5 The pseudopotential approximation

The electrons in an atom can be divided into two types — core electrons and valence electrons. The core electrons are tightly bound to the nucleus, while the valence electrons are more extended. A working definition for core electrons is that they are the ones which play no part in the interactions between atoms, while the valence electrons dictate most of the properties of the material. It is common to make the frozen core approximation. The core electrons are constrained not to differ from their free atomic nature when placed in the solid state environment. This reduces the number of electronic degrees of freedom in an all electron calculation. It is a very good approximation. A different, but physically related, approach is taken in the pseudopotential approximation[13, 7].

Since, in an all electron calculation, the valence electron wavefunctions must be orthogonal to the core wavefunctions they necessarily have strong oscillations in the region near the nucleus (see the all electron wavefunction in Figure 3). Given that a planewave basis set is to be used to describe the wavefunctions, these strong oscillations are undesirable — requiring many plane waves for an accurate description. Further, these oscillations are of very little consequence for the electronic structure in the solid, since they occur close to the nucleus, and interact little with the neighbouring atoms. In the pseudopotential approach only the valence electrons are explicitly considered, the effects of the core electrons being integrated within a new ionic potential. The valence wavefunctions need no longer be orthogonal to the core states, and so the orthogonality oscillations disappear, hence far fewer plane waves are required to describe the valence wavefunctions. This modified ionic potential, or pseudopotential, is constructed in the following way. An all electron DFT calculation is performed for an isolated atom. A core radius r_c is decided upon — chosen so that the core regions of neighbouring atoms will not overlap. The smaller the core radius the greater the transferability of the pseudopotential (i.e. the more chemical environments it will be valid in). The all electron valence wavefunctions are altered within r_c to remove the nodal structure. These new functions are the pseudowavefunctions. The Schrödinger equation is then inverted to find the potential that would produce these wavefunctions — this is the pseudopotential. See Figure 3 for a schematic representation of the potentials and wavefunctions (pseudo and true). It is usual to ensure that the charge within the core radius is the same for the pseudo and true wavefunctions — this is known as norm-conservation

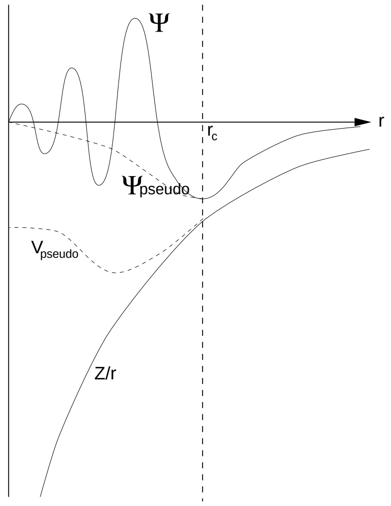

Figure 3: A schematic representation of the pseudopotential and pseudowavefunction. Not that the wavefunctions and potentials agree beyond the core radius, r_c and that the pseudowavefunctions are considerably smoother than the true wavefunctions within r_c — reducing the number of planewaves required.

and simplifies many aspects of the implementation of pseudopotentials and also improves the energy range over which the pseudopotential is valid [12]. Since a pseudopotential must reproduce the correct phase shifts on scattering at the core, and these phase shifts will be different for different angular momentum states, in general a pseudopotential will be non-local, with different projectors for different angular momentum components.

In this work the non-local pseudopotentials are in the Kleinman-Bylander form[18]:

$$V = V_{loc} + \sum_{l,m} (V_l - V_{loc}) \hat{P}_{l,m}, \tag{16}$$

where the choice of V_{loc} is arbitrary. Using the approach of Lee [20], in some cases the potentials can be projector reduced. This consists of constructing two of the V_l to be very similar — both being eliminated by a single careful choice of V_{loc}. The method of Lee *et al* [21] has also been applied to optimise the pseudowavefunction with respect to planewave cutoff.

1.6 Minimisation of the energy functional

Equation 9 shows that the total energy functional can be minimised by solving a Schrödinger-like eigenvalue problem for a set of single particle wavefunctions $\{\phi_i : i = 1, N\}$. Clearly, standard matrix-diagonalisation techniques could be used, but it is highly inefficient in the case of a planewave approach. There are many more planewaves per atom than electronic states required. If M is the number of planewaves in a calculation, then typically $M/N > 100$. Hence, diagonalising a $M \times M$ matrix results in M eigenstates while only the lowest N are required. As an alternative, the total energy functional is minimised using the idea first proposed by Car and Parinello [3], the actual minimisation using a preconditioned conjugate gradient technique [24, 30]. These methods are implemented in the program CASTEP (CAmbridge Serial Total Energy Package).

1.7 Forces, Stresses and Structural Optimisation

While the evaluation of single point total energies is useful in the investigation of atomic structures, the real power of this ab initio method is only evident when it is realized that the quantum mechanical forces can be found. Feynman and Hellman independently showed how this could be done - using what is now known as the Hellman-Feynman theorem [8]. In a similar way, the quantum mechanical stresses on the unit cell of a periodic crystal can be evaluated. Once these forces and stresses are available then the problem becomes like any other in structural optimisation. Real dynamics can be used, thus allowing first principles molecular dynamics to be performed, or a fictitious dynamics invented to accelerate geometrical optimisation.

2 Bandstructure from the total energy method

It is well known that the Kohn-Sham eigenstates resulting from the diagonalisation of the Hamiltonian in Equation 9 do not formally correspond to the single particle states required in the evaluation of the optical properties[16]. It should be remembered that they were simply introduced as a tool for dealing with the kinetic energy term in the functional $F[n(\mathbf{r})]$; while is was convenient that the result was a mapping of the many-body problem onto one for single particles, those single particle states need not have any physical meaning. However, it is nearly universal to interpret these unoccupied

Kohn-Sham eigenstates as the excited states required for our purposes, and with good reason. In many cases, where this interpretation is made, very good agreement is found between theory and experiment. It has been shown by Godby *et al* [10] that, for Silicon at least, the difference between the Kohn-Sham excitation energies and the correct quasiparticle energies can be summarised by a rigid shift of the conduction band upwards with respect to the valence band, the wavefunctions themselves being essentially unchanged. This rigid shift, or "scissor operator", is irrelevant for the calculation of ELNES at the current level of theory since the absolute energy of the threshold is not calculated. Reviews of the connection between DFT and excitation energies are presented by Godby [9] and Jones and Gunnarsson [16].

Clearly, when a total energy calculation is performed there is no need to evaluate the unoccupied eigenstates — only the valence states contribute to the total energy. But, the calculation of spectral properties often requires the unoccupied states. So, in practice two calculations are performed. In the first the self consistent ground-state charge density is found, and then a subsequent calculation is performed using the fixed Hamiltonian resulting from that charge density. Many more eigenstates are found, at many more **k**-points, since accurate Brillouin zone integrations are required.

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