# INTERATOMIC FORCES

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by

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## Preface

If we make the broad divisions between ionic, covalent and metallic systems the only practical method of total energy and force calculation which works in the same way for each is the *Hohenberg-Kohn-Sham density functional theory*, an *ab initio* (or first principles) approach which assumes as input only the charges on the nuclei and their positions. Because of its computational cost it is not practical to do all the simulations one might like with a first principles scheme, although the improvements in algorithms and computers over the past few years have greatly extended the range of problems which can indeed be tackled in this way. There are however many more approximate but faster schemes of calculation which are of use in materials science.

In these notes I wish to show how various such approximate schemes of total energy and force calculation, usually regarded as empirical or semi-empirical in nature, can be derived from the same first principles approach, namely the Hohenberg-Kohn-Sham theory. You will not find any useful information here about the *implemention* of any schemes; for that you will have to go to the literature and the manuals of computer programs. This is rather an attempt at an overview of the *principles* of different schemes. The schemes I will discuss are:

- The empirical tight binding model, which has been applied to transition metals, semiconductors and their alloys. In particular I describe a self-consistent tight-binding scheme which I recently developed with Tony Paxton [9,8] for partially covalent oxides.
- The Effective Medium, Embedded Atom, Finnis-Sinclair, Second Moment or Glue Models, which are in their form (if not in their derivation) simplified forms of tight-binding and which have been used for large simulations of metallic systems. At the time of writing I regard a "large" simulation for a metal on a work station as about 100K atoms. Simulations of over 100M atoms have been done on parallel computers.
- The ionic model, including polarisible ions.
- Pair-potentials, which can be justified for simple (s-p bonded) metals.

My selection and treatment of these schemes is personal (in the sense that they are schemes I happen to have worked with myself) and not exhaustive, so I risk annoying people whose favourite scheme is not discussed. Sorry if you are one of them; please compose an excuse from my lacks of time, knowledge, intelligence and memory.

My presentation is rather more unified than usual, but also briefer. The reader who has not studied elementary quantum mechanics will find it hard going. For anyone curious to know more I have recommended a number of books and articles, the most general being refs. [4], [10], [18], [19], [26], [28] and [36].

## A Note on Units and Conventions

I use Hartree atomic units, in which the unit of length is the Bohr radius (0.5292 Å), the unit of charge is the electronic charge ($e$) and the unit of mass is the electronic mass. Planck's constant $\hbar$ is unity and the unit of energy is the Hartree (27.212 *eV*). Many other authors use the Rydberg (13.606 *eV*) as the unit of energy . The main confusion which can arise is in expressions for the electrostatic energy of some system of charges: because in Rydberg units $e^2 = 2$.

Wavefunctions of a single electron are written in Dirac "bra-ket" notation as $|\psi\rangle$. As a function of position **r** the wavefunction is written $\langle \mathbf{r}|\psi\rangle \equiv \psi(\mathbf{r})$. The scalar product of two wavefunctions $|\psi_1\rangle$ and $|\psi_2\rangle$ is written $\langle \psi_1|\psi_2\rangle$ and interpreted as the integral over all space

$\int \psi_1^*(\mathbf{r})\psi_2(\mathbf{r})d\mathbf{r}$, where $d\mathbf{r}$ is a volume element.

A factor of two is included by some authors to count the up and down spin electrons which occupy a "single" wavefunction. I have preferred to suppress the spin index on the wavefunction, that means to include it implicitly in the index *nk*, so there are no explicit extra factors of 2 for double occupancy, for example in equation (1.3) below for the charge density obtained by summing over occupied states. I do not discuss the effect of magnetism, which would require an explicit notation for spin.

The spherical harmonics used here are real. As described by Stone [33], for $m \neq 0$ these are symmetric and antisymmetric combinations of the conventional, complex spherical harmonics:

$$\begin{aligned} Y^c_{lm} &= (-1)^m 2^{-\frac{1}{2}}(Y_{lm} + Y^*_{lm}) \\ Y^s_{lm} &= -(-1)^m i\, 2^{-\frac{1}{2}}(Y_{lm} - Y^*_{lm}) \end{aligned}$$

In the notes the suffix $L$ is used for the combined indices $l$ and $m$, and we suppress the suffices $c$ and $s$. The normalisation for the complex spherical harmonics here is the standard one described in Jackson [23], p.99, rather than the one used by Stone.

## 1. The Hohenberg-Kohn-Sham background

I give here a summary of the Hohenberg-Kohn-Sham (HKS) results, which are the tools for applying density functional theory to the calculation of total energies and interatomic forces. A standard reference is the book by Parr and Yang [26]. You will find a discussion of all the subtle points there. I do little more here than define notation.

The key quantity in density functional theory is the electron density $n(\mathbf{r})$, in terms of which the standard HKS functional for the total energy of a system of electrons and ions at zero absolute temperature can be written as

$$\begin{aligned} E^{HKS} &= T_s[n] \\ &\quad + \int nV^c d\mathbf{r} + \tfrac{1}{2}\int nV^H[n] d\mathbf{r} + E^{xc}[n] \quad . \\ &\quad + E^{cc} \end{aligned} \tag{1.1}$$

The first term is the kinetic energy which the electrons in the system would have with this density, supposing them to be non-interacting; this is therefore the sum of single-particle kinetic energies:

$$T_s = \sum_{nk}^{occ} \left\langle \psi^{nk} \middle| \tfrac{1}{2}\nabla^2 \middle| \psi^{nk} \right\rangle \tag{1.2}$$

where the summation runs over a set of occupied *single particle wave functions* which are labelled by their $k$-vector and band index $n$. These labels are appropriate for systems which are infinite and periodic, in which calculations are done by applying periodic boundary conditions to atoms in a box. In finite (bounded) systems the *k*-vector is not a good quantum number, so for generality simply regard *nk* as a label. There is implicitly a summation over both up and down spins which I have subsumed in the index *n*. The great achievement of Kohn and Sham was this way of treating a major part of the kinetic energy, by referring to a hypothetical system of non-interacting electrons with the same density as the real system.

Note at this point that the electron density is expressed in terms of the single particle wave functions as in Hartree-Fock theory by:

$$n(\mathbf{r}) = \sum_{n,k}^{occ} \left|\psi^{nk}(\mathbf{r})\right|^2 . \tag{1.3}$$

The second term in (1.1) is the interaction between electrons and cores. By “cores” I mean either ions or nuclei. Some explanation of this concept is appropriate. For many calculations, the inner shell electrons are not relevant to the properties of the material, whose bonding depends on the outer electrons (valence or conduction electrons), and these inner shell, or core electrons can be lumped together with the nucleus forming an ion and making a total core potential. The core potentials behave like an external potential felt by the remaining electrons which are treated explicitly in the calculation. This division of the electrons is carried out in the *pseudopotential* methods, discussed later. Returning to (1.1), the third term is the Hartree electrostatic self-energy of the electrons, in which the Hartree potential of the electrons appears. It is given by

$$V^{H}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|} d\mathbf{r}' \ . \tag{1.4}$$

The fourth term is the exchange and correlation energy. It actually also includes that part of the true many-body kinetic energy of the electrons which has not been correctly counted by $T_s$. Within the local density approximation (LDA) it is represented by a local function $\varepsilon^{xc}(n)$ of the electron density:

$$E^{xc}[n] = \int n\varepsilon^{xc}(n)\,d\mathbf{r}\,. \tag{1.5}$$

In applications the approximation (1.5) is usually made, because the local function $\varepsilon^{xc}$ is the exchange and correlation energy per electron of a homogeneous electron gas, and this has been calculated and tabulated. However the LDA is not assumed in the development of the formalism here unless explicitly stated. Unfortunately no exact formula for the exchange and correlation energy of an *in*homogeneous electron gas is known; nevertheless eqn.(1.5) has proved to be remarkably accurate for many materials. There are notable exceptions among the transition metal oxides. Magnetic materials also require a different treatment, but in many cases they can be handled in an analogous way by defining separate up and down spin densities.

Finally, the last term in (1.1) is the core-core interaction, which is a classical sum of Coulomb interactions, completely independent of the electron density:

$$E^{cc} = \tfrac{1}{2}\sum_{i\neq j}\frac{Z_i Z_j}{R_{ij}} \quad . \tag{1.6}$$

This term is included here for the completeness of the total energy. It is often omitted from the functional because it is not relevant to calculating the electronic structure and electron density for fixed positions of the ions.

The HKS functional is minimised with respect to the charge density $n$ to get the ground state total energy. The minimisation is at constant total number of electrons $N$:

$$N = \int n\,d\mathbf{r} \ . \tag{1.7}$$

The resulting Euler-Lagrange equation, known as the Kohn-Sham equation, is a single particle Schrödinger equation for each single particle wave function:

$$\left(-\tfrac{1}{2}\nabla^2 + V^{eff}\right)\left|\psi^{nk}\right\rangle = \varepsilon_{nk}\left|\psi^{nk}\right\rangle \quad , \tag{1.8}$$

where $V^{eff}$ is the effective single particle potential and is given by

$$V^{eff} = V^{c} + V^{H} + V^{xc} \quad . \tag{1.9}$$

In (1.9), $V^{c}$ is the potential of the ions, $V^{H}$ is the Hartree potential given by (1.4) and $V^{xc}$ is the exchange and correlation potential, given by the functional derivative of the exchange and correlation energy:

$$V^{xc}(\mathbf{r}) = \frac{\delta E^{xc}[n]}{\delta n(\mathbf{r})} \quad . \tag{1.10}$$

In (1.1) and (1.2) the wave functions and charge density are always implicitly linked via eqn.(1.3).

A slightly different way to write the HKS functional, by rearranging (1.1), is

$$\begin{aligned} E^{HKS} = &\sum_{n,k}^{occ} \left\langle \psi^{nk} \right| -\tfrac{1}{2}\nabla^2 + V^{eff} \left| \psi^{nk} \right\rangle \\ &-\int n V^{eff}[n]\, d\mathbf{r} + \int n V^{c}(\mathbf{r})\, d\mathbf{r} + \tfrac{1}{2}\int n V^{H}[n]\, d\mathbf{r} + E^{xc}[n] \\ &+E^{cc} \end{aligned} \tag{1.11}$$

This form has been very fruitful for further approximations. For by the variational principle for the Kohn-Sham equation (1.8), in the ground state the first term in (1.11) is variationally minimised with respect to the wave functions at fixed $V^{eff}$, that is at fixed charge density. It then becomes just the sum of the lowest $N$ Kohn-Sham eigenvalues $\varepsilon^{nk}$. This can be interpreted as a sum over the occupied single particle states, or the N states of lowest energy. The meaning of the energies of these states must be interpreted with caution, since they are not the eigenvalues of the many electron Hamiltonian.

In this way we can conceptually decouple the wave functions and the charge density and regard the functional as depending on them independently, without the automatic link which eqn.(1.3) has provided up to now. The functional is then variationally extreme with respect to both. It is even possible to go a step further and to decouple $V^{eff}$ in the same way, regarding $E^{HKS}$ as a function of the wave functions, the charge density and the effective potential as if these three kinds of quantities were independent. This may be useful because $E^{HKS}$ is a variational extreme, although not a minimum, with respect to all three [20].

## 2. The Kohn-Sham functional to second order

The functional is expanded about some reference charge density, $n_0$, which is arbitrary but should be in some sense a useful approximation to the true charge density. Typically it would be the superposition of atomic charge densities. I will also use the subscript 0 to denote quantities derived from $n_0$, such as the Hartree potential $V_0^H$. The charge density will now be characterised by its deviation $\delta n = n - n_0$, which I assume to be small. The functional becomes:

$$\begin{aligned} E^{HKS} = &\sum_{n,k}^{occ} \left\langle \psi^{nk} \right| -\tfrac{1}{2}\nabla^2 + V_0^{eff} \left| \psi^{nk} \right\rangle - \int (n_0 + \delta n) V^{eff}[n_0]\, d\mathbf{r} \\ &+ \int (n_0 + \delta n) V^c d\mathbf{r} + \tfrac{1}{2} \int (n_0 + \delta n) V^H [n_0 + \delta n]\, d\mathbf{r} + E^{xc}[n_0 + \delta n] \\ &+ E^{cc} \quad . \end{aligned} \tag{2.1}$$

Now make a Taylor expansion of (2.1) to second order in $\delta n$. Note first that

$$E^{xc}[n_0 + \delta n] = E_0^{xc} + \int \delta n\, V_0^{xc}\, d\mathbf{r} + \tfrac{1}{2} \iint \delta n\, \delta n' \frac{\delta^2 E^{xc}}{\delta n\, \delta n'} d\mathbf{r}\, d\mathbf{r}' \cdots \tag{2.2}$$

where $\delta n'$ is short for $\delta n(\mathbf{r}')$. The first order terms sum to zero and after substituting for $V^{eff}[n_0]$ from (1.9) we are left with:

$$\begin{aligned} E_2^{HKS} = &\sum_{n,k}^{occ} \left\langle \psi^{nk} \right| -\tfrac{1}{2}\nabla^2 + V_0^{eff} \left| \psi^{nk} \right\rangle \\ &+ E^{cc} - \tfrac{1}{2} \int n_0 V_0^H d\mathbf{r} + E^{xc}[n_0] - \int n_0 V_0^{xc} d\mathbf{r} \\ &+ \tfrac{1}{2} \iint \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E^{xc}}{\delta n \delta n'} \right) \delta n\, \delta n'\, d\mathbf{r}\, d\mathbf{r}' \end{aligned} \tag{2.3}$$

and this is a useful starting point for further approximations, as first shown explicitly by Frauenheim and coworkers [7].

As it stands, $E_2^{HKS}$ in eqn.(2.3) is no more convenient than the original $E^{HKS}$in eqn.(1.11) for making calculations, because in either case an iterative procedure is required. First an input charge density must be guessed (e.g. $n_0$), then the Kohn-Sham equation (1.8) has to be solved for the eigenvalues and single particle wave functions, then the electron density must be constructed from these output wave functions according to (1.3). Finally the charge density must be updated in some way before repeating the cycle, and so on until some convergence criterion is met when the input and output charge densities are the same to sufficient accuracy and $E^{HKS}$ (or $E_2^{HKS}$ ) has then been minimised. Unlike $E^{HKS}$, $E_2^{HKS}$ in the ground state is not variationally minimised with respect to the $\left|\psi^{nk}\right\rangle$ independently of the charge density; that would be too good to be true! Unfortunately, in (2.3) the wavefunctions and charge density must be coupled in the usual way for application of the variational principle. This coupling gives a Kohn-Sham equation as follows.

**The first order Kohn-Sham equation**

To apply the variational principle to (2.3), first express $\delta n$ in terms of the wavefunctions, then make a small variation in $\left\langle\psi^{nk}\right|$:

$$\delta n = \sum_{nk}^{occ} \left\langle \psi^{nk} \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \psi^{nk} \right\rangle - n_0 \tag{2.4}$$

and

$$\begin{aligned} 0 = \delta E_2^{HKS} = & \left\langle \delta\psi^{nk} \right| -\tfrac{1}{2}\nabla^2 + V_0^{eff} \left| \psi^{nk} \right\rangle \\ & + \tfrac{1}{2} \iint \Big( K(\mathbf{r},\mathbf{r}') \sum_{nk}^{occ} \Big( \left\langle \delta\psi^{nk} \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \psi^{nk} \right\rangle \delta n' + n \left\langle \delta\psi^{nk} \middle| \mathbf{r}' \right\rangle \left\langle \mathbf{r}' \middle| \psi^{nk} \right\rangle \Big) d\mathbf{r}\, d\mathbf{r}' \end{aligned} \tag{2.5}$$

where I have defined the kernel

$$K(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \left.\frac{\delta^2 E^{xc}}{\delta n\, \delta n'}\right|_{\{n,n'\}\in n_0} . \tag{2.6}$$

The variation in the ket is superfluous, since the operators are Hermitian. Hence

$$\begin{aligned} 0 = & \left\langle \delta\psi^{nk} \right| -\tfrac{1}{2}\nabla^2 + V_0^{eff} \left| \psi^{nk} \right\rangle \\ & + \int \left\langle \delta\psi^{nk} \middle| \mathbf{r} \right\rangle \Big( \int K(\mathbf{r},\mathbf{r}') \delta n'\, d\mathbf{r}' \Big) \left\langle \mathbf{r} \middle| \psi^{nk} \right\rangle d\mathbf{r} \end{aligned} . \tag{2.7}$$

Since the wavefunction variation is arbitrary but subject to maintaining orthonormality of the occupied wavefunctions, eqn.(2.7) is equivalent to the Kohn-Sham equation:

$$\left(-\tfrac{1}{2}\nabla^2 + V_0^{eff}(\mathbf{r}) + \int K(\mathbf{r},\mathbf{r}')\delta n'\,d\mathbf{r}'\right)\langle\mathbf{r}|\psi^{nk}\rangle = \varepsilon_{nk}\langle\mathbf{r}|\psi^{nk}\rangle \quad . \tag{2.8}$$

The kernel $K$ combines the Hartree, exchange and correlation contributions to the effective potential from the first order self-consistent change in the electron density.

## 3. The Harris-Foulkes Functional

The Harris-Foulkes functional [17,14] is obtained by omitting the second order terms from $E_2^{HKS}$:

$$\begin{aligned} E^{HF} &= \sum_{n,k}^{occ} \langle\psi^{nk}| -\tfrac{1}{2}\nabla^2 + V_0^{eff} |\psi^{nk}\rangle \\ &\quad + E^{cc} - \tfrac{1}{2}\int n_0 V_0^H d\mathbf{r} + E^{xc}[n_0] - \int n_0 V_0^{xc} d\mathbf{r} \quad . \end{aligned} \tag{3.1}$$

It must be variationally minimised with respect only to the $|\psi^{nk}\rangle$, since there are no other terms in (3.1) that depend on the charge density; remember the input density $n_0$ is held fixed. This does not require any iterations to self-consistency of the kind I described above, just the solution of the Kohn-Sham equation for the wave functions in the potential $V_0^{eff}$. The quality of the Harris-Foulkes approximation compared to the full functional depends entirely on how accurately the input charge density $n_0$ reproduces the self-consistent charge density $n$ which would have resulted from the minimisation of $E^{HKS}$. The error in the energy so obtained is evidently of second order in $\delta n$, so the functional $E^{HF}$ is stationary with respect to $\delta n$. At one time it was conjectured that $E^{HF}$ is variationally maximal with respect to $n_0$ and equal to $E^{HKS}$ at the variational minimum of the latter. It has since been established [32], however, that although $E^{HF}$ is *stationary* at $n_0 = n$, where $n$ is the density that minimises $E^{HKS}$, it is certainly neither maximum nor minimum. Athough it is a pity we don't have this bounding propoerty, $E^{HF}$ is nevertheless a useful approximation, particularly as a basis further simplifications such as the tight-binding model [37].

### Hellmann-Feynman Forces

The stationary property of the HKS functional with respect to *n* also gives us immediately the simple result for the forces on the nuclei, often called the Hellmann-Feynman theorem. Suppose we move an ion infinitesimally, changing thereby the external potential on the electrons by $\delta V^c$. The unperturbed ground state charge density is $n_0$. It is trivial to show that the total change in energy of the ground state is given to first order by:

$$\delta E^{HKS} = \delta E^{HF} = \int n_0 \delta V^c + \delta E^{cc} \ . \tag{3.2}$$

Equation (3.2) is a very useful result, and a startling one when you first meet it. It is exactly what the change in classical electrostatic energy due to the given movement of the ion would be if the electron density were held fixed. It therefore tells us that once we have the ground state charge density, the forces on nuclei can be calculated with classical electrostatics. This is implemented in nearly all atomistic simulation programs.

## 4. Empirical tight binding models

### Non self-consistent tight binding

The Harris-Foulkes functional has been used as a basis for further approximations leading to a tight-binding model [37]. The wave functions are expanded in localised orbitals labelled by their angular quantum numbers centred on the atomic sites *R*

$$\left|\psi^{nk}\right\rangle = \sum_{RL} c_{RL}^{nk} \left|\varphi^{RL}\right\rangle \ . \tag{4.1}$$

The localised orbitals can be written in the form

$$\left\langle \mathbf{r} \middle| \varphi^{RL} \right\rangle = f_{R\,l}\left(\left|\mathbf{r}-\mathbf{R}\right|\right) Y_L(\mathbf{r}-\mathbf{R}) \tag{4.2}$$

where the $Y_L \equiv Y_{lm}$ are spherical harmonics.

The electron density is therefore

$$n(\mathbf{r}) = \sum_{nk}^{occ} \sum_{RL\,R'L'} c_{RL}^{nk*} c_{R'L'}^{nk} \left\langle \varphi^{RL} \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \varphi^{R'L'} \right\rangle \ . \tag{4.3}$$

If we define the reference Hamiltonian by $H_0$, where

$$\langle \mathbf{r}|H_0|\mathbf{r}\rangle = -\tfrac{1}{2}\nabla^2 + V_0^{eff}(\mathbf{r}) \tag{4.4}$$

the Harris-Foulkes form of the Kohn-Sham equation is

$$H_0\left|\psi^{nk}\right\rangle = \varepsilon_{nk}\left|\psi^{nk}\right\rangle \quad . \tag{4.5}$$

Now by substituting (4.1) into (4.5) and premultiplying by one of the localised basis orbitals $\left\langle\varphi^{RL}\right|$ we obtain the matrix eigenvalue equations:

$$\sum_{R'L'}\left\langle\varphi^{RL}\left|H_0\right|\varphi^{R'L'}\right\rangle c_{R'L'}^{nk} = \varepsilon_{nk}\sum_{R'L'}\left\langle\varphi^{RL}\middle|\varphi^{R'L'}\right\rangle c_{R'L'}^{nk} \quad . \tag{4.6}$$

In empirical forms of tight binding, the matrix elements are free parameters to be fitted. Tony Paxton and I, like many before us, fitted them to the band structure calculated by a fully first-principles method. No functional forms for the orbitals themselves are introduced. Furthermore it is common to assume as we did that three centre integrals can be neglected, which means that the matrix elements in (4.6) do not depend on the coordinates of atoms besides the pair $R$ and $R'$. This is probably the most serious approximation of the entire theory. A further simplification is to assume that the local basis orbitals are orthonormal, so that the right hand side of (4.6) is a single term. At this level of approximation, the remaining terms in the total energy, which are given in the second line of (3.1), are approximated by pairwise potentials between the atoms, e.g. of Born-Mayer form, which are fitted to data such as the lattice parameter and bulk modulus. The total energy from (3.1) then takes the semi-empirical form:

$$E^{HF} \to E^{TB} = \sum_{n,k}^{occ}\left\langle\psi^{nk}\left|H_0\right|\psi^{nk}\right\rangle + \tfrac{1}{2}\sum_{RR'}V^{pair}\left(\left|\mathbf{R}-\mathbf{R}'\right|\right) \quad . \tag{4.7}$$

When this has been minimised with respect to the wavefunctions, by solving the Kohn-Sham-Schrödinger equation, the first term becomes the sum of the eigenvalues of the occupied wavefunctions, or

$$E^{TB} = \sum_{nk}^{occ}\varepsilon_{nk} + \tfrac{1}{2}\sum_{RR'}V^{pair}\left(\left|\mathbf{R}-\mathbf{R}'\right|\right) \quad . \tag{4.8}$$

**Self-consistency**

Self-consistency is included within the tight binding framework by solving eqn.(2.8) in an iterative cycle

$$\delta n^{in} \to \left\{ \left| \psi^{nk} \right\rangle \right\} \to \delta n^{out} .$$

A local basis is used as before, but now there is a part of the Hamiltonian, $H'$, that must be updated at each cycle of iteration. We write the total Hamiltonian as

$$H = H_0 + H' \quad . \tag{4.9}$$

The matrix form of the Kohn-Sham equation with orthogonal orbitals is

$$\sum_{R'L'} \left\langle \varphi^{RL} \right| H_0 + H' \left| \varphi^{R'L'} \right\rangle c^{nk}_{R'L'} = \varepsilon_{nk}\, c^{nk}_{R'L'} \tag{4.10}$$

and there are now some new matrix elements which must be specified:

$$\left\langle \varphi^{RL} \right| H' \left| \varphi^{R'L'} \right\rangle = \int \left\langle \varphi^{RL} \middle| \mathbf{r} \right\rangle \int K(\mathbf{r},\mathbf{r}')\, \delta n' d\mathbf{r}' \left\langle \mathbf{r} \middle| \varphi^{R'L'} \right\rangle d\mathbf{r} \quad . \tag{4.11}$$

Eqn.(4.10) has to be solved repeatedly until convergence is achieved, when

$$\delta n^{in} = \delta n^{out} \quad .$$

In order to specify the matrix elements in (4.11) further approximations are made. Firstly we neglect three-centre integrals, that is, when $R \neq R'$ we neglect integrals involving a contribution to $\delta n'$ by a site which is neither $R$ nor $R'$.

The contributions to $\delta n'$ made by $R$ and $R'$ when $R \neq R'$ are:

$$\delta n'^{R} = \sum_{nkL''L'''}^{occ} c^{nk*}_{RL''}\, c^{nk}_{RL'''} \left\langle \varphi^{nk}_{RL''} \middle| \mathbf{r}' \right\rangle \left\langle \mathbf{r}' \middle| \varphi^{nk}_{RL'''} \right\rangle - n_0^{R} \tag{4.12}$$

$$\delta n'^{R'} = \sum_{nkL''L'''}^{occ} c^{nk*}_{R'L''}\, c^{nk}_{R'L'''} \left\langle \varphi^{nk}_{R'L''} \middle| \mathbf{r}' \right\rangle \left\langle \mathbf{r}' \middle| \varphi^{nk}_{R'L'''} \right\rangle - n_0^{R'} \tag{4.13}$$

$$\delta n'^{RR'} = \sum_{nkL''L'''}^{occ} c^{nk*}_{RL''}\, c^{nk}_{R'L'''} \left\langle \varphi^{nk}_{RL''} \middle| \mathbf{r}' \right\rangle \left\langle \mathbf{r}' \middle| \varphi^{nk}_{R'L'''} \right\rangle + c.c. \tag{4.14}$$

in which *c.c.* denotes the complex conjugate of the terms which precede it and $n_0^{R}$ and $n_0^{R'}$ are the input electron densities at $r'$ contributed by atoms at $R$ and $R'$ respectively. The next level of approximation is to neglect intersite matrix elements of $H'$, so that only on-site elements of $\delta n'$ contribute.

**On-site matrix elements**

In order to evaluate the matrix elements of the variable part of the Hamiltonian, $H'$, from eqn.(4.11), we shall need not only the local orbital representation of the charge density as given by (4.12)-(4.14), but also the local orbital representation of the kernel $K(\mathbf{r},\mathbf{r}')$. At this point we meet a dilemma. The natural thing to do would be to introduce the expansion:

$$K(\mathbf{r},\mathbf{r}') = \sum_{RL\,R'L'} \langle \mathbf{r} | \varphi^{RL} \rangle K_{RL\,R'L'} \langle \varphi^{R'L'} | \mathbf{r}' \rangle \quad , \tag{4.15}$$

however this would only be correct if the localised basis were complete. It certainly is not complete if in the basis there is only one representative of each angular momentum on each site, the commonly used *minimal basis* approximation. This problem is apparent if we consider the Coulomb part of the kernel $K^H(\mathbf{r},\mathbf{r}') = 1 / |\mathbf{r}-\mathbf{r}'|$.

A pure Coulomb interaction defined by $1/|\mathbf{r}-\mathbf{r}'|$ has the well-known expansion in spherical harmonics that is given in Jackson (1975), equation 3.70:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = 4\pi \sum_L \frac{1}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_L(\mathbf{r}) Y_L(\mathbf{r}') \tag{4.16}$$

where $r_>$ is the greater and $r_<$ is the smaller of $r$ and $r'$. With our choice of a minimal basis, eqn.(4.16) is incompatible with (4.15); however we *can* use (4.16) directly when $R$ and $R'$ are well apart, and in this case it is surely preferable to (4.15). For in this case the exchange and correlation contribution to $K$, let us call it $K^{xc}$, becomes negligible compared to the Coulomb interaction $K^H$ and we can evaluate the potential near $R$ by the classical solution of the Laplace equation for multipoles contributed by $\delta n$ centred at $R'$. Thus we are led to the approximation of treating all the intersite contributions to $K$ as the Coulomb potentials of multipoles. This introduces an error in the contribution of the

Coulomb part of $K$ because of the overlapping charge densities of nearest neighbours. Furthermore by ignoring the contribution of $K^{xc} = \delta^2 E^{xc} / \delta n \delta n'$ when $\mathbf{r}$ and $\mathbf{r}'$ are different we are making the *local density approximation* (LDA) for exchange and correlation. The latter error is not a serious one in the energetics of many materials, including oxides of simple metals and early transition metals. Despite the fact that it omits for example the van der Waals interaction between anions in ionic crystals, the LDA gives a good account of the energetics of alkali halides and simple metal oxides. As for the former error, the hope is that even if it is not small it is somehow swept up by the empirical pair potential.

I now define a *multipole* of the change in electron density $\delta n^R$ by

$$Q^e_{RL} = \sum_{nk\,L'L''}^{occ} \int d\mathbf{r}\, r^l\, Y_L(\mathbf{r}) \left( c^{nk*}_{RL''} c^{nk}_{RL'''} \left\langle \varphi^{RL''} \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \varphi^{RL'''} \right\rangle - n^R_0(\mathbf{r}) \right) . \tag{4.17}$$

It is equivalent to the expectation value of the multiple operator [33] with the omission of intersite matrix elements.

This can be expressed immediately in terms of *strength parameters*

$$\Delta^R_{l\,l'l''} = \int dr\, r^{2+l} f_{Rl'}(r) f_{Rl''}(r) \tag{4.18}$$

which are specific to our system, and the well known Gaunt coefficients

$$C_{L\,L'L''} = \iint d\Omega\, Y_L Y_{L'} Y_{L''} \tag{4.19}$$

that determine selection rules, as follows:

$$Q^e_{RL} = \sum_{nk\,L'L''}^{occ} c^{nk*}_{RL'} c^{nk}_{RL''}\, \Delta^R_{l\,l'l''}\, C_{L\,L'L''} - \delta_{L0}\, q^R_0 / (4\pi)^{\frac{1}{2}} . \tag{4.20}$$

I have introduced $q^R_0$ which is the total number of input electrons on atom $R$.

$$q^R_0 = \int d\mathbf{r}\, n^R_0(\mathbf{r}) . \tag{4.21}$$

The potential at $\mathbf{r}$ near $R$ , meaning that part of the potential which has non vanishing matrix elements with the local orbitals at $R$, can now be expressed as an on-site term arising from $\delta n^R$, which is discussed later, and the sum of contributions from each $\delta n^{R'}$ where $R' \neq R$. These latter contributions are

$$V_R(\mathbf{r}) = \sum_{R' \neq R} \int \frac{\delta n^{R'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{4.22}$$

which by inserting (4.16) and (4.17) can be written as follows:

$$V_R(\mathbf{r}) = 4\pi \sum_{R' \neq R} \sum_{L} \frac{1}{(2l+1)} \frac{1}{|\mathbf{r} - \mathbf{R}'|^{l+1}} Y_L(\mathbf{r} - \mathbf{R}') Q^e_{R'L} \quad . \tag{4.23}$$

In order to evaluate the matrix elements of $V_R(\mathbf{r})$ between orbitals on the site $R$ we first make an expansion of it in spherical harmonics:

$$V_R(\mathbf{r}) = \sum_{L} V_{RL}\, r^l\, Y_L(\mathbf{r}) \quad . \tag{4.24}$$

The coefficients $V_{RL}$ can be obtained by applying the expansion theorem of a static multipole field to eqn.(4.23). The result can be written in the form

$$V_{RL} = \sum_{R' \neq R} B_{L L'}(\mathbf{R}' - \mathbf{R}) Q^e_{R'L'} \tag{4.25}$$

where
$$B_{L L'}(\mathbf{R}' - \mathbf{R}) = \frac{(4\pi)^2}{(2l+1)!!(2l'+1)!!} \sum_{L''} (-1)^{l'} C_{L L' L''} \frac{(2l''-1)!!}{|\mathbf{R}' - \mathbf{R}|^{l''+1}} Y_{L''}(\mathbf{R}' - \mathbf{R}) \quad . \tag{4.26}$$

In terms of its expansion coefficients (2.1) and the delta coefficients defined in (4.18) the matrix elements of the potential in (4.24) can be written immediately as:

$$\left\langle \varphi^{R L'} \middle| V_R \middle| \varphi^{R L''} \right\rangle = \sum_{L} V_{RL}\, \Delta^R_{L' L'' L}\, C_{L' L'' L} \quad . \tag{4.27}$$

Finally consider the contribution to the on-site matrix elements at $R$ from $\delta n^R$. In principle a large number of terms should be taken into account, however in practice these have been lumped into a single term for each $L$:

$$U_l \int d\mathbf{r} \delta n^R_l(\mathbf{r}) = U \delta q^R_l, \tag{4.28}$$

where $U_l$ is an empirical constant (sometimes called "the Hubbard $U$"), $\delta n^R_l$ is the contribution to $\delta n^R$ (see eqn. (4.12)) from the orbitals of symmetry $L$ and $\delta q^R_l$ is the change in the number of electrons on the atom at **R** contributed by the orbitals of symmetry *L*. In practice so far the possible *l* dependence of *U* has been ignored.

The total energy within this self-consistent tight-binding (SCTB) scheme can be written down by adding to the functional (4.7) the appropriate second order term corresponding to the above approximations for *K*. The final result is:

$$E^{SCTB} = \sum_{n,k}^{occ} \left\langle \psi^{nk} \,|\, H_0 \, |\psi^{nk} \right\rangle + \tfrac{1}{2} \sum_{RR'} V^{pair}\left(|\mathbf{R} - \mathbf{R}'|\right) + \tfrac{1}{2} \sum_{RL} \left( U_l \left(\delta q_l^R\right)^2 + Q_{RL}^e V_{RL} \right). \quad (4.29)$$

Self-consistent tight-binding can be implemented more crudely than the description above implies. At the simplest level of self-consistent tight-binding, only $U\delta n^R$ terms are included (the *l* dependence is ignored) and no account is taken of changes in other matrix elements. In particular, matrix elements between orbitals on a site are ignored. The next level of complexity, which is the level described above, is to include the *L*>0 or "crystal field" terms, i.e. changes in the matrix elements between orbitals on a site. No one has deemed it worthwhile yet to include self-consistency in inter-site matrix elements. Possibly the reason is that this would introduce so many more parameters that the simplicity of empirical tight-binding would have been lost, as well as its computational efficiency. When too many parameters have to be fitted there is a higher risk of producing an unphysical model. Probably at least the crystal field terms are necessary in partially ionic materials such as oxides, but the level of sophistication actually required is a matter for ongoing research.

### The tight-binding bond model

The concept of the tight-binding bond model [37] is linked to the idea that in metals there is very little charge transfer. A tight-binding model with precisely zero charge transfer (neutral atoms) is equivalent to self-consistent tight binding with $U = \infty$. If the atoms remain neutral, it is reasonable to assume that the on-site elements of the Hamiltonian do not contribute to changes in the energy when the atoms are moved around.

In practice this is implemented by varying the on-site matrix elements in a self-consistency cycle to achieve charge neutrality of the atoms. The resulting diagonal terms in the sum of one electron energies (the first sum in (4.8)) are subtracted out, so that the sum of one electron energies becomes a sum of inter-site matrix elements or *bond energies*. Details of this approach are given in the reference [37]. Non self-consistent tight-banding which retains the diagonal elements of the Hamiltonian, as described previously, is sometimes called the tight-binding *band* model. The tight-binding bond model is a more consistent way to describe the energies of atoms in different configurations than the band model, because the approximation of neutral atoms is often a very good one.

## 5. Second moment models and the like

The starting point for models in this category is the Harris-Foulkes functional. Here I show how the simplest model for metals, which I will call the second-moment model (SMM), is derived. Some of the earlier work on this subject is in the references [2,3]. There are many variants of this model, the parameters of which are fitted to experimental data for bulk metals [11,1,38,22,40]. A rather similar model is derived by the effective medium theory (EMT) [34,25,29,24], which takes as its zeroth order the energy of an atom which is immersed in an electron gas of the appropriate local electron density, the meaning of “appropriate” here being open to more than one interpretation. The term “embedded atom model” (EAM) is also commonly used generically for such SMM and EMT-type models, and it will be convenient here to use the term EAM in this way, although it was first used for the empirical type of EMT developed by Daw, Baskes, Foiles and coworkers [5,13].

The form of these EAMs depends on the definition of a certain local ‘density’ ρ (not necessarily the electron density; see below) which is defined at an atomic site *i* by summing a pair function $\phi(R_{ij})$ over the neighbours *j* of *i* :

$$\rho_i = \sum_j \phi(R_{ij}) \ . \tag{5.1}$$

The range of $\phi$ is usually restricted to two or three shells of neighbours.

The total energy is the the sum over atoms of a function of $\rho_i$, which provides the attractive forces between the atoms (causing their cohesion), and a pairwise repulsion:

$$E^{EAM} = \sum_i f_i(\rho_i) + \tfrac{1}{2}\sum_{i \neq j} V^{pair}\left(R_{ij}\right) \ . \tag{5.2}$$

**Derivation of a Second Moment Model**

To see how a SMM, and other approximations to the full TB model, can be derived, let us look a bit deeper into the formalism. More details and depth can be found in the books [21,4]. In extended systems, because the single particle energies form a practically continuous spectrum, the sum over occupied states is usually written (and calculated) as the integral over the *density of states*: so that the non self-consistent tight binding energy, eqn. (4.8), becomes:

$$E^{TB} = \int_{-\infty}^{\varepsilon_F} \varepsilon n(\varepsilon) d\varepsilon + \tfrac{1}{2}\sum_{i \neq j} V^{pair}\left(R_{ij}\right) \ . \tag{5.3}$$

where the density of states is given by:

$$n(\varepsilon) = \sum_{nk} \delta\left(\varepsilon - \varepsilon_{nk}\right) \ . \tag{5.4}$$

The Fermi energy $\varepsilon_F$ has been introduced, together with the fairly accurate assumption of zero temperature.

If the basis is orthonormal, which we assume for simplicity, this can also be expressed as

$$n(\varepsilon) = \sum_{nk} \sum_{RL} c_{RL}^{nk*} c_{RL}^{nk} \delta\left(\varepsilon - \varepsilon_{nk}\right) \ . \tag{5.5}$$

By reversing the order of summation in (5.5) we can express the density of states as a sum of local densities of states:

$$n(\varepsilon) = \sum_R n_R(\varepsilon) \ , \tag{5.6}$$

where

$$n_R(\varepsilon) = \sum_L \sum_{nk} c_{RL}^{nk*} c_{RL}^{nk} \delta(\varepsilon - \varepsilon_{nk}) \ . \tag{5.7}$$

The key quantity in the SMM is the second moment of the local density of states:

$$\mu_{2R} = \int_{-\infty}^{\infty} \varepsilon^2 n_R(\varepsilon) d\varepsilon = \sum_L \sum_{nk} c_{RL}^{nk*} c_{RL}^{nk} \varepsilon_{nk}^2 \ , \tag{5.8}$$

which is a component of the second moment of the *total* density of states:

$$\mu_2 = \sum_{nk} \varepsilon_{nk}^2 \tag{5.9}$$

The idea is to approximate the first term of (5.3) (called the *band energy*) by using only a knowledge of the $\mu_{2R}$ for the current configuration of atoms, and this turns out to give the EAM form of the cohesive part of the energy.

It is done as follows. We can write the square of an eigenvalue $\varepsilon_{nk}$ in terms of the Hamiltonian:

$$\varepsilon_{nk}^2 = \left\langle \psi^{nk} \middle| H^2 \middle| \psi^{nk} \right\rangle \ . \tag{5.10}$$

Now use the completeness identities

$$\sum_{RL} \left| \varphi^{RL} \right\rangle \left\langle \varphi^{RL} \right| = 1; \quad \sum_{nk} \left| \psi^{nk} \right\rangle \left\langle \psi^{nk} \right| = 1 \ , \tag{5.11}$$

inserting them between the factors in (5.10) to obtain

$$\mu_2 = \sum_{nk} \varepsilon_{nk}^2 = \sum_{RR'} \sum_{LL'} \left| \left\langle \varphi^{RL} \middle| H \middle| \varphi^{R'L'} \right\rangle \right|^2 = \sum_R \mu_{2R} \ . \tag{5.12}$$

where

$$\mu_{2R} = \sum_{R'} \sum_{LL'} \left| \left\langle \varphi^{RL} \middle| H \middle| \varphi^{R'L'} \right\rangle \right|^2 \ . \tag{5.13}$$

The SMM makes the approximation that the integral $\int_{-\infty}^{\varepsilon_F} \varepsilon n_R(\varepsilon) d\varepsilon$ is proportional to $(\mu_{2R})^{\frac{1}{2}}$:

$$\int_{-\infty}^{\varepsilon_F} \varepsilon n_R(\varepsilon) d\varepsilon = A(\mu_{2R})^{\frac{1}{2}} \ . \qquad (5.14)$$

This is would be exactly true if

a) The shape of the local density of states remains the same while it is stretched or compressed along the energy axis as a result of the local environment,

b) The charge on the atom is fixed (the neutral atom model).

The substitution of (5.14) and (5.13) into (5.3) leads directly to the form (5.2), if the further assumption is made that the Hamiltonian matrix elements have no angular dependence; that is, they are like the matrix elements between *s*-orbitals.

## 6. Ionic models

The ionic model as developed by Max Born and coworkers and expounded in several text books is an intuitive description of the cohesion of ionic crystals, but one which we can be rigourously derived. It proceeds first by creating ions in their standard valence states, in which they have closed shells of outer s and p electrons, and then bringing them together to form a crystal. The energy of cohesion of the crystal is mainly due to the electrostatic attraction of the oppositely charged ions as they are brought together, known as the Madelung energy. The ions are regarded as point charges, or non-overlapping charged spheres and the infinite Coulomb summations to obtain the Madelung energy can be done by rapidly convergent methods which are now standard. For ordered binary compounds it takes the form

$$E_{Mad} = -\alpha(\eta_1 + \eta_2) Z_1 Z_2 / 2d \ . \qquad (6.1)$$

where $\eta_1$ and $\eta_2$ are the numbers of atoms in a formula unit $Z_1$ and $Z_2$ are the charges on the ions, $d$ is the cation-anion distance and $\alpha$ is the Madelung constant, which has been calculated for many common crystal structures. For disordered or strained structures it is calculated routinely by standard methods.

The remaining repulsive part of the energy is due to overlap of the electronic charge distributions and was traditionally calculated by including an empirical pairwise repulsive term $V^{pair}(|\mathbf{R}-\mathbf{R}'|)$ between the ions, for example of the Born-Mayer or Lennard-Jones form:

$$V^{pair}(R)=4\varepsilon\left(\left(\frac{\sigma}{R}\right)^{12}-\left(\frac{\sigma}{R}\right)^{6}\right). \tag{6.2}$$

The parameters of this could be adjusted to fit the experimental cohesive energy and lattice parameter.

The resulting total energy is:

$$E=\tfrac{1}{2}\sum_{i\neq j}\frac{Z_iZ_j}{R_{ij}}+\tfrac{1}{2}\sum_{i\neq j}V^{pair}\left(R_{ij}\right), \tag{6.3}$$

where I have used the same notation as in eqn.(1.6), since the Madelung energy is just the same as the core-core energy in that equation if the core electrons are treated as frozen.

Successful calculations based on the ionic model have also been made with no adjustable parameters by a method refined by Gordon and Kim [15], in which $V^{pair}(|\mathbf{R}-\mathbf{R}'|)$is obtained by calculating the total energy of the electrons in a dimer, where the electron density is assumed to be a superposition of the electron densities of the separate ions at $\mathbf{R}$ and $\mathbf{R}'$. This calculation is done with a local density approximation for the kinetic energy, besides the exchange and correlation energies. Subsequently, Hartree-Fock calculations have been made for the dimers, to remove doubts in the local approximations of the Gordon-Kim calculations, which tend to underestimate the repulsive strength of the interactions [31]. The pairwise additive nature of the energy of an assembly of closed shell atoms is justified by the empirical success of the Lennard-Jones model of rare gases, besides its qualified success in calculating the properties of ionic systems. However, non-pairwise forces do contribute significantly to the elastic constants of ionic materials, or materials that are consideret to be mainly ionic, such as MgO. In all cubic materials, non-pairwise forces are the reason for deviations from the Cauchy relation $C_{12} = C_{44}$. Such deviations are the rule rather than exceptions.

A further indication of the pairwise additive nature of the energy when closed shells of electrons are involved in only one of the species comes from first-principles density functional calculations of the energy of noble gas atoms embedded in a free electron gas (jellium). It is found that the energy is to a good approximation linear as a function of the undisturbed electron density of the jellium [30].

So far I have been completely vague about the origin of the repulsive force in (6.3) due to overlapping electron densities of the ions. It includes the direct electrostatic interaction as well as quantum mechanical exchange. We can however be completely explicit by considering the tight binding form of the HKS equations as described in Section 4. Within that framework, an ionic model is characterised by having negligible matrix elements of the Hamiltonian between different sites.

There are a number of extensions to the simple ionic model described above, most of which are inspired by the original shell model [6], to include the polarisability of the ions, particularly the anions. In oxides it has been shown that polarisability at dipolar and quadrupolar levels is necessary to understand the energy differences between different crystal structures [39]. In addition, in the modern ionic models, an additional parameter is associated with the anion to describe its state of compression or expansion; the compressibility of anions has also been shown to have a decisive effect on the relative energies of structures. Regarding the Cauchy discrepancy, a model with dipole polarisable anions is still forced by the cubic symmetry to predict $C_{12} = C_{44}$, becase the dipoles remain zero under homogeneous strains, but the compressible shell model is not so constrained.

A recent interesting development in empirical ionic models is the inclusion of charge transfer as a classical variable [35], which seems to be shortcutting the tight-binding treatment of this effect in which a Schrödinger equation has to be solved. This is an area of ongoing research.

In terms of the SCTB model, we can recover an ionic model with dipole and quadrupole polarisability: this is the result if the on-site matrix elements linking different orbitals are retained, but without any *intersite* matrix elements. However, this does not seem like a useful way in practice to derive an ionic model. A dipolar or quadrupolar charge density on an anion arises when electrons on a site redistribute between the available local orbitals. There is an effect of this kind as the electrons redistribute between the 2*p*-orbitals in oxygen for example, but to make it realistic more orbitals must be added. However, some of the charge redistribution may be better described by including intersite matrix elements and thus modelling variable charge transfer, than by adding more orbitals to the basis. Furthermore without any intersite matrix elements we might as well implement a classical model of the dipole and quadrupole polarisabilities.

## 7. Pair potentials in simple metals

Pair potentials in simple metals were derived back in the sixties without reference to the emerging HKS theory. They rely on the concept of *pseudopotentials*, which is still very much alive in the field of first principles HKS calculations. The traditional theory of pseudopotentials has been dealt with exhaustively in books [18,16] and review articles, and I make only the briefest summary of it here.

### Pseudopotentials

It was noticed long ago that simple metals such as Na, Mg and Al have electronic properties which can be described as if the electrons are nearly free. In the completely free electron model there are no discrete atoms and the conduction electrons move on a uniform distribution of positive charge; that is the *jellium* model. In the real metal the positive background charge is replaced by discrete ions, with charges 1, 2 and 3 for Na, Mg and Al respectively. These are centres of strong Coulomb attraction, consisting of nuclei surrounded by closed shells of core electrons. Nevertheless their effect on the conduction electrons can be treated as a weak perturbation to the conduction electrons. This paradoxical situation was resolved by the introduction of pseudopotentials. Pseudopotentials then took on a far more important role in the understanding and computation of electronic structure.

Electrons moving through the metal are scattered by an effective potential from each ion. We can describe how an electron is scattered, which incidentally depends on its energy, in different ways. One way is to generate the wave functions that are solutions of the Schrödinger equation at some energies for a single free atom or ion. If we draw a sphere of radius $R_c$ around the ion, and agree only to generate the correct wavefunction outside it, we will have a perfectly adequate description of the atom for the purposes of chemical bonding and interatomic forces *if* $R_c$ *is small enough.* This is so even if we get the wavefunction inside $R_c$ completely wrong. A wavefunction which is correct outside $R_c$ but fictitious inside $R_c$ is called a *pseudowavefunction*. The forces between atoms cannot depend on the antics of electrons within $R_c$ if their wavefunction is correctly specified in the region outside $R_c$, assuming that the total charge density of the ion inside $R_c$ is spherically symmetric. In other words if we specify correctly how electrons are scattered from spheres of radius $R_c$ about each ion, we have provided all the information needed to generate the forces between the atoms, at least in principle.

The next step is to notice that the potential within $R_c$ which gives rise to a particular wavefunction outside $R_c$ is not unique! In fact we can replace the real potential of the core, which behaves like $-Z/r$ at short range, by a much weaker potential which has the same effect. The weaker potential, which is the pseudopotential of this ion, will not bind states to the core, but otherwise it will scatter electrons of higher energy in the same way as the real potential. The core radius $R_c$ is somewhat arbitrary. Choose it too big and the chemical bonding may be poorly modelled. Choose it too small and the pseudopotential is no longer so weak. In practice $R_c$ may depend on the angular momentum quantum number $l$ of the scattered electron; the pseudopotential itself, as it turned out, *has* to depend on $l$ to construct an accurate model. The construction of pseudopotentials is done by solving for the potential in the Schrödinger equation, having specified a pseudowavefunction. It is something of an art, which I will not attempt to describe here. The important point is that the pseudowavefunction can be chosen to be smooth within $R_c$, whereas the real wavefunction would have wiggles in it.

While the angular momentum dependence (*non-locality*) of pseudopotentials is important in practice, it is not relevant to a discussion of the principles, so I shall ignore it the following.

Pseudopotentials are nowadays widely used for first-principles total energy and force calculations, because (a) the core electrons are not treated explicitly, saving computation time, and (b) the pseudowavefunctions, because they are chosen to be relatively smooth within $R_c$, can be expanded in much fewer plane waves than would be necessary for the corresponding real wavefunctions. The computational advantage of expanding a wavefunction in plane waves are well known [27]; the fewer variables (the expansion coefficients) which have to be obtained by a selfconsistent iterative procedure the faster the solution can be found.

The property of pseudopotentials that they weakly scatter electrons is central for deriving a pairwise potential description of the bonding, which is computationally the simplest description one could want. This is only reasonable for *s-p* bonded metals; the *d*-orbitals in transition metals cannot be treated as inner core orbitals, because they participate in the bonding, neither are they smooth enough for the electrons in *d*-orbitals to be treated as nearly free.

## Linear screening

Pair potentials were derived and applied in the sixties and early seventies to describe the properties of simple metals [18]. The following is a simple derivation of pairwise potentials.

Given a weak pseudopotential $V^{ps}(\mathbf{r})$, the response of the electron gas to it can be described by linear screening as:

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r},\mathbf{r}')V^{ps}(\mathbf{r}')\,d\mathbf{r}'. \tag{7.1}$$

Due to translational symmetry, the response function has the form:

$$\chi(\mathbf{r},\mathbf{r}') \equiv \chi(|\mathbf{r}-\mathbf{r}'|)\ . \tag{7.2}$$

This static response function is fairly well known and is usually referred to in its reciprocal space form as the Fourier transform of (7.2), $\chi(\mathbf{q})$, and it depends on the density of the jellium via the Fermi wavevector $k_F = \left(3\pi^2 n_0\right)^{\frac{1}{3}}$. In general it can be expressed in terms of the dielectric screening constant $\varepsilon(\mathbf{q})$ as

$$\varepsilon^{-1} = 1 + 4\pi\chi / q^2\ . \tag{7.3}$$

This follows from the definition of the screening constant as the ratio between the external and the total potentials, or

$$V^{ps} + 4\pi\delta n / q^2 = \varepsilon^{-1}\cdot V^{ps}\ . \tag{7.4}$$

The factor $4\pi / q^2$ is the Fourier transform of the Coulomb potential of an electron.

The response function $\chi$ can be related to $\chi_0$, which is that of a hypothetical system of non-interacting electrons (Kohn and Sham’s reference system again). This goes as follows. Equation (7.1) can be written as

$$\delta n = \chi_0\left(V^{ps} + (1-G)4\pi\delta n / q^2\right) \tag{7.5}$$

where the terms in brackets are the change in *effective* potential in the Kohn-Sham sense. The quantity $G$, which depends on $q$, is included to represent the correction for exchange and correlation. Eliminating $\delta n$ from (7.5) and (7.1), which can be wrutten as $\delta n = \chi \delta V^{ps}$, gives

$$\chi = \frac{\chi_0}{1-(1-G)4\pi\chi_0 / q^2} \ . \tag{7.6}$$

If exchange and correlation are ignored, there is an exact expression for $\varepsilon(\mathbf{q})$ which is due to Lindhardt:

$$\varepsilon^L(\mathbf{q}) = 1 + \frac{4\pi k_F}{q^2}\left[\frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right], \quad x = \frac{q}{2k_F} \ . \tag{7.7}$$

The change in total energy which is brought about by switching on the ions in jellium can be calculated from (3.2). We suppose that the pseudopotentials are switched on adiabatically such that the pseudopotential at a certain stage in the process is given by $\lambda V^{ps}$, where the parameter $\lambda$ is switched continuously from 0 to 1. From (3.2) the energy change is

$$E_2^{HKS} - E_0^{HKS} = E^{cc} + \int_0^1 d\lambda \int (n_0 + \lambda \delta n) V^{ps} = E^{cc} + \int n_0 V^{ps} + \tfrac{1}{2}\int \delta n V^{ps} \, . \tag{7.8}$$

To make contact with (2.3) we can write (7.8) in terms of the inverse response function defined by

$$V^{ps}(\mathbf{r}) = \int \chi^{-1}(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}')d\mathbf{r}' \tag{7.9}$$

giving

$$E_2^{HKS} = E_0^{HKS} + E^{cc} + \int n_0 V^{ps} + \tfrac{1}{2}\int \delta n(\mathbf{r})\chi^{-1}(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}') \ . \tag{7.10}$$

where

$$E_0^{HKS} = T_0[n_0] + E^{xc}[n_0] \, , \tag{7.11}$$

We can write (2.3) in yet another form, making the kinetic energy explicit and expanding it to second order about the uniform electron gas (the first order term vanishes by translational symmetry):

$$
\begin{aligned}
E_2^{HKS} &= T[n_0] + \tfrac{1}{2}\iint \delta n \frac{\delta^2 T}{\delta n \delta n'} \delta n' + \int n V^{ps} \\
&\quad + E^{cc} - \tfrac{1}{2}\int n_0 V_0^H + E^{xc}[n_0] \\
&\quad + \tfrac{1}{2}\iint \delta n K \delta n'.
\end{aligned}
\tag{7.12}
$$

Formally minimising with respect to *n* we get

$$
\int \frac{\delta^2 T}{\delta n \delta n'} \delta n' + V^{ps} + \int K \delta n' = 0 \ . \tag{7.13}
$$

Comparing with (7.9) we identify:

$$
\chi^{-1} = -\frac{\delta^2 T}{\delta n \delta n'} - K \ . \tag{7.14}
$$

Furthermore for a hypothetical system of non-interacting electrons, $K = 0$. For the non-interacting system the response function is therefore defined by

$$
\chi_0^{-1} = -\frac{\delta^2 T}{\delta n \delta n'} \tag{7.15}
$$

evaluated in the uniform electron gas.

Hence we find the relationship

$$
\chi^{-1} = \chi_0^{-1} - K \ . \tag{7.16}
$$

This is consistent with the expression (7.6), in Fourier space, in which the kernel *K* appears as the Coulomb interaction reduced by the factor (1-*G*) for exchange and correlation.

**The pair potentials**

The potential $V^{ps}$ in (7.8) is a sum of contributions from each ion:

$$
V^{ps} = \sum_R V_R^{ps}(\mathbf{r} - \mathbf{R}) \ . \tag{7.17}
$$

Because of the linear nature of the response of the electrons, the electron density can also be decomposed in an obvious way into contributions, which screen each ion:

$$\delta n(\mathbf{r}) = \sum_R \int \chi(\mathbf{r},\mathbf{r}')V^{ps}(\mathbf{r}'-\mathbf{R})d\mathbf{r}' = \sum_R \delta n_R \tag{7.18}$$

where

$$\delta n_R(\mathbf{r}) = \int \chi(\mathbf{r},\mathbf{r}')V_R^{ps}(\mathbf{r}'-\mathbf{R})d\mathbf{r}'. \tag{7.19}$$

In this way the second order term in the energy can be written as a sum of pairwise interactions between the ions:

$$\tfrac{1}{2}\int \delta n V^{ps} = \tfrac{1}{2}\sum_{R,R'} V_{RR'} \tag{7.20}$$

where

$$V_{RR'} = \int \delta n_R(\mathbf{r})V_{R'}^{ps}(\mathbf{r}-\mathbf{R}')d\mathbf{r}\ . \tag{7.21}$$

We can think of this as the electrostatic interaction between one ion and the screening charge induced by another. Since the pseudopotentials and the charges they induce are spherically symmetric, the potential $V_{RR'}$ is also a pure pair potential $V\left(|\mathbf{R}-\mathbf{R}'|\right)$. The term when $R = R'$ is like a self-energy and is insensitive to the crystal structure. These self-energy terms and the rest of the energy in (7.10), which does not depend on the crystal structure, nevertheless depend on the density of the material, because they depend on $n_0$. The pair potential itself also depends on $n_0$ because the response function depends on $n_0$.

**Peculiarities of the pair potentials**

From the previous results, we see that the total energy of a simple metal can be written as a function of its average density plus a sum of pairwise functions which are also a function of the average density. We can summarise the situation as:

$$E = F(n_0) + \tfrac{1}{2}\sum_{R,R'} V(|\mathbf{R}-\mathbf{R}'|;n_0)\ . \tag{7.22}$$

The linear screening approximation will break down if the density of the material is inhomogeneous. An extreme case for illustrative purposes would be a surface. Imagine a macroscopic box containing equal volumes of solid and vapour separated by a planar surface. It would be a very poor approximation to use formula (7.22) with $n_0$ as the mean density of electrons in the box, because this density would be half as much as the appropriate value for the solid. However, the derivation above requires the mean value of $n_0$ for the whole system, and there is no obvious way to do better. It has long been known that would be essential to do better than this in order to describe the energy not only of surfaces but even of single vacancies. An *ad hoc* solution which may provide a semi-empirical model would be to keep the form (7.22) but to define the density in some *local* way. This has been discussed in detail recently [12] but not yet implemented in a simulation code.

Before leaving the subject of pair potentials it is worth comparing the total energy in the form (7.22) with the embedded atom (EAM) form of the total energy. The formal differences are:

- The density, which is an argument of the *pseudopotential* pair potential, does not appear in the *EAM* pair potential at all.
- The density in the EAM is a local quantity, sometimes thought of as the density formed by overlapping the charge densities of atoms at other sites. As discussed above, in the pseudopotential approach on the other hand, the density means the average density of the whole system, and is therefore non-local, which is unphysical for systems which are inhomogeneous.
- The pair potential in the pseudopotential theory is long ranged. This is because of the logarithmic singularity in the screening function in reciprocal space at $q = 2k_F$ which gives rise to oscillations in real space in the screening function and therefore the pair potential. The decay of the pair potential to zero can be accelerated by including the effect of temperature, which spreads the electrons about the Fermi energy and smooths out the singularity in (7.7). However, the decay is still generally slower than

the EAM potentials, the functions in which are usually constructed to vanish after second or third shells of neighbours.

Although even for simple metals the pair potentials based on pseudopotentententials are out of fashion, and EAM potentials are more widely used, my guess is that with the interest in light aluminium-lithium-magnesium based alloys, and the possibility of including the density dependence in a local way, pseudopotentials may return to favour in special cases. They have the great advantage of requiring fewer parameters to be fitted.

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