Bond-order potentials through the ages

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Abstract

Bond-order potentials are an appealing way to describe the cohesive energy of materials, because they are based on the rigorous quantum mechanics of electrons, they can be derived for semiconductors as well as transition metals, and they are suitable for large scale atomistic simulations, yielding insights that previous, simpler models of interatomic forces could not. The concept grew out of Coulson's definition of bond orders in molecules published in 1939, and was developed into a workable scheme by David Pettifor and co-workers, starting in the 1980s. This article is an introduction to the ideas and their implementation.

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1. Introduction

When I was at school we learned that a carbon atom forms a single bond with each hydrogen atom in methane, and a single bond with another carbon atom in ethane, whereas it can form a double bond with another carbon atom in ethylene and even a triple bond in acetylene. Just what these double and triple bonds might mean was mysterious to me at the time, although we did learn that triple bonds were stronger than double bonds that were stronger than single bonds. It was many years later that I learned how bond orders, as these numbers one, two and three for single, double and triple bonds are called, can be calculated. Pauling, Lennard-Jones, Penney, Coulson and others had been seeking a satisfactory quantitative definition of the 'order of a bond' as it was called during the 1930s, in the days when nouns were less easily used as adjectives. It was first derived on a satisfactory basis from the point of view of molecular orbital theory by Coulson himself and published in 1939 [1]. Coulson's approach, which is essentially the concept we use today, went further by showing how fractional bond orders should be defined in a natural way to deal with conjugated molecules. In the same paper, he showed how the sum of occupied orbital energies, expressed in terms of bond orders, could be combined with a central pairwise potential to predict the equilibrium bond-lengths in hydrocarbon molecules. This was only a little cruder than modern empirical tight-binding, and of course Coulson did not have a computer.

Nevertheless, although the calculation of bond orders provided a qualitative index of bond strength, it did not give a quantitative measure of the energy of bonds that could be applied for atomistic simulation of solids. Between Coulson's idea of a bond order and David Pettifor's idea of a bond-order *potential* [2], which did just that, 50 years elapsed. That it took so long to turn the qualitative description of a chemical bond in terms of a single number, its bond order, into the quantitative description of its energy within different structures, tells us that quite a lot of solid-state physics had to be done in the meantime. But even if the theory of bond-order potentials had been worked out earlier, the computer power to exploit them for atomistic simulations had scarcely arrived before the 1990.

In this paper, I will introduce the physics of bond-order potentials and the approaches used to compute them. It should serve as an introduction for those unfamiliar with the concept, and in particular as background to the advances and the applications described by the following authors. A more comprehensive description of the theory in the wider context of models for atomistic simulation is given in Ref. [3]. For a clear introduction to the concepts of tight-binding, which is the foundation for bond-order potentials, there is the book by Sutton [4].

Mainly for the uninitiated let us start by defining some quantities and give the simplest example. We work here within a description in terms of independent electrons such as Kohn–Sham density functional theory [5] and expand states in localised orbitals $\phi_{I\mu}$, where μ labels a state centred on atom I which is at position $\mathbf{R}_I$. The eigenstates of the one-electron Hamiltonian $\widehat{H}$ are labeled in order of energy by integers n such that ψ_0 is the lowest in energy. The expansion coefficients for the eigenstates of the Hamiltonian are $C_n^{I\mu}$, where

$$\psi_n = \sum_{I\mu} C_n^{I\mu} \phi_{I\mu}. \tag{1}$$

The eigenstates form an orthonormal complete set. Normally, the local orbitals are chosen to be real functions, although this is not essential. The basis states form a complete set, but not necessarily an orthonormal one, and there is a matrix $\mathbf{S}$ with elements

$$S_{I\mu J\nu} \equiv \int \phi_{I\mu}^*(\mathbf{r}) \phi_{J\nu}(\mathbf{r}) \, d\mathbf{r} \tag{2}$$

which in an orthonormal basis is just the identity matrix $\mathbf{1}$ with elements $\delta_{I\mu J\nu}$. The $\mathbf{S}$-matrix can therefore be written as the sum of $\mathbf{1}$ and a matrix $\mathbf{O}$ that explicitly describes the non-orthogonality:

$$\mathbf{S} = \mathbf{1} + \mathbf{O}. \tag{3}$$

The Schrödinger (or Kohn–Sham) equation in the local basis is

$$\sum_{J\nu} H_{I\mu J\nu} C_n^{J\nu} = \epsilon_n \sum_{J\nu} S_{I\mu J\nu} C_n^{J\nu} \tag{4}$$

in which the Hamiltonian matrix elements are

$$H_{I\mu J\nu} = \int \phi_{I\mu}^*(\mathbf{r}) \widehat{H}(\mathbf{r}) \phi_{J\nu}(\mathbf{r}) \, d\mathbf{r}. \tag{5}$$

The normalisation of the nth eigenstate means that for each n the coefficients $\{C_n^{I\mu}\}$ must satisfy

$$\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) \, d\mathbf{r} = \sum_{I\mu J\nu} C_n^{I\mu} C_n^{J\nu*} S_{J\nu I\mu} = 1, \tag{6}$$

which we obtain by inserting the eigenstate expansion (1). While we imagine here the system to be finite, the extension to periodic, infinite solids is fairly straightforward: an additional index k must be added, and the basis functions are Bloch sums of the local orbitals.

Now let the occupancies of these eigenstates be f_n. Let ϵ_n be the energy of the nth eigenstate. All states with energies ϵ_n lower than the energy of the highest occupied molecular orbital (in solids this corresponds to the Fermi energy ϵ_F) are occupied by two electrons of opposite spin. The assumption that the electrons have zero temperature is usually adequate in this context of total energy calculation. For the highest occupied molecular orbital itself f_n might take a smaller value if the orbital is degenerate, otherwise it is also 2. For all the higher states $f_n = 0$ by definition. We shall also write the occupancy of a state with energy ϵ as

$$f(\epsilon) \equiv 2f_F(\epsilon), \tag{7}$$

where $f_F(\epsilon)$ is the usual Fermi function.

With the above notation for expansion coefficients and occupancies, the bond order between orbital μ on atom I and orbital v on atom $J \neq I$ is defined as

$$\Theta^{I\mu J v} = \sum_{n=0}^{\infty} \frac{1}{2} f_n \big(C_n^{I\mu} C_n^{J v*} + c.c. \big), \quad I \neq J. \tag{8}$$

The notation *c.c.* means the complex conjugate of the preceding term. Strictly speaking, this is a *partial* bond order until it has been summed over all the orbitals belonging to a particular bond or within a particular representation of the symmetry operator. In the usual nomenclature nowadays the full bond might for example be a π-bond, orientated along the z-axis, in which case orbitals of p_x and p_y type on each atom would be summed over to obtain the total π-bond order.

In the modern theory of solids the wavefunctions, at least in crystals, are characterised and labelled by their k-vector. Their energy eigenvalue is labelled by its *band* index. If these two labels are considered to be subsumed in the above label n, the above formula for bond orders in molecules applies to bond orders in infinite crystalline solids. There is an important difference in the nature of the summations over n, because the k-vector part of that is a summation over all the k-vectors within the Brillouin zone. There are infinitely many, but they have a characteristic density in k-space and the summation becomes an integral over the occupied part of the Brillouin zone, which in real calculations has to be handled by some kind of sampling method. For quantitative calculations on real solids even Coulson would have needed a computer at this point.

1.1. Example: bond orders for beginners

The simplest case that illustrates the concept is a diatomic molecule, with one s-orbital on each atom. The eigenstates are bonding and antibonding combinations:

$$\begin{aligned} \psi_0 &= \frac{1}{\sqrt{2}} (\phi_{Is} + \phi_{Js}), \\ \psi_1 &= \frac{1}{\sqrt{2}} (\phi_{Is} - \phi_{Js}). \end{aligned} \tag{9}$$

With one electron this represents the H_2^+ molecule, and applying (8) with $f_0 = 1$ and $f_1 = 0$ gives its bond order:

$$\Theta^{IsJs} = \frac{1}{2}.$$

With two electrons we have the H_2 molecule, $f_0 = 2$ and $f_1 = 0$ and its bond order:

$$\Theta^{IsJs} = 1.$$

Adding a further two electrons would be a crude model of He_2, with $f_0 = 2$ and $f_1 = 2$. The partial bond orders of the bonding and antibonding states in this case are 1 and -1, so the total bond order is

$$\Theta^{IsJs} = 0.$$

Writing down the formula (8) for general occupancies reveals that the total bond order is proportional to the difference in the occupancy of the bonding and antibonding states:

$$\Theta^{I\mu Jv} = \frac{1}{2}(f_0 - f_1).\tag{10}$$

This is a rather general result, although the signs depend on the particular symmetry of the orbitals. For example if we are looking at a p_z orbital on each atom, in which the positive lobes are always in the positive z-direction, the bonding state is the *difference* in the orbitals and the higher energy antibonding state is their sum, so formula (10) is reversed in sign.

Eq. (10) gives us a qualitative understanding of how the definition of the bond order is appropriate for characterising the bond energy. Let us now explore the quantitative link between bond order and energy.

2. The strength of a bond

2.1. The density operator

The concept of a bond order can be considered as a daughter of the concept of a density matrix. The density matrix in turn is derived from the density operator $\hat{\rho}$ defined by

$$\hat{\rho} = \sum_{n=0}^{\infty} |n\rangle f_n \langle n|.\tag{11}$$

The wavefunctions ψ_n are written here in Dirac's vector notation [6] as "state vectors" so that they are independent of the basis orbitals and whether they are localised or delocalised. This notation is also explained and used extensively in [3]. In Dirac notation the localised basis orbitals in (1) are

$$\phi_{I\mu}(\mathbf{r}) \equiv \langle \mathbf{r}|I_\mu\rangle\tag{12}$$

and one uses the language of linear algebra to think of $\phi_{I\mu}(\mathbf{r})$ as like the projection of the vector $|I\mu\rangle$ in the space on the vector $|\mathbf{r}\rangle$, or the scalar product of these two vectors. Expanding the state vectors in (11) in terms of our local basis, for which the expansion coefficients are defined in (1), we have an alternative expression for the density operator:

$$\hat{\rho} = \sum_{I\mu Jv} \left| I\mu \right\rangle \sum_{n=0}^{\infty} f_n C_n^{I\mu} C_n^{Jv*} \left\rangle Jv \right|.\tag{13}$$

Defining the expansion coefficient

$$\rho^{I\mu Jv} \equiv \sum_{n=0}^{\infty} f_n C_n^{I\mu} C_n^{Jv*}\tag{14}$$

the density operator can be written as

$$\hat{\rho} = \sum_{I\mu Jv} |I\mu\rangle \rho^{I\mu Jv} \langle Jv|.\tag{15}$$

Comparing (14) with (8) we see that a partial bond order is nothing other than an intersite expansion coefficient of the symmetrised density operator:

$$\Theta^{I\mu Jv} \equiv \frac{1}{2}(\rho^{I\mu Jv} + c.c.) \equiv \frac{1}{2}(\rho^{I\mu Jv} + \rho^{Jv I\mu}).\tag{16}$$

In general, the *expansion coefficient* $\rho^{I\mu J\nu}$ is not the same as the corresponding *matrix element* of the density operator, namely

$$\rho_{I\mu J\nu} \equiv \langle I\mu|\hat{\rho}|J\nu\rangle, \tag{17}$$

except when the basis set $\{—I\mu\rangle\}$ is orthonormal. For that reason suffices are used here to indicate a matrix element and superfices to indicate an expansion coefficient. The often-used term "density matrix" is ambiguous in this respect, but it is a convenient shorthand when the context is clear.

One of the useful properties of the density operator is its *trace*, which gives us the total number of electrons N. The trace of an operator $\widehat{A}$ is defined as

$$\text{Tr}\widehat{A} = \sum_{n=0}^{\infty} \langle n|\widehat{A}|n\rangle. \tag{18}$$

The value of $\text{Tr}\widehat{A}$ evaluated according to (18) is the same for any complete and orthonormal set of basis vectors $\{|n\rangle\}$, they would not have to be the eigenfunctions of $\widehat{H}$ although that might be the most convenient choice. Applying (18) to (11) produces the total number of electrons:

$$\text{Tr}\hat{\rho} = \sum_{n=0}^{\infty} f_n = N. \tag{19}$$

Now take the trace of $\hat{\rho}$ in the form (15), this time using the basis $\{|\mathbf{r}\rangle\}$, for which the sum is replaced by an integral:

$$\text{Tr}\hat{\rho} = \sum_{I\mu J\nu} \int \langle \mathbf{r}|I\mu\rangle \rho^{I\mu J\nu} \langle J\nu|\mathbf{r}\rangle \, \mathrm{d}\mathbf{r} = \sum_{I\mu J\nu} \rho^{I\mu J\nu} S_{J\nu I\mu}. \tag{20}$$

Equating these two expressions for $\text{Tr}\hat{\rho}$ gives us

$$N = \sum_{I\mu J\nu} \rho^{I\mu J\nu} S_{J\nu I\mu}. \tag{21}$$

The relation (21) suggests a natural way to define the number of electrons on each site, which is required for calculating charge transfers. Picking out the $I\mu$ terms we define the number of electrons associated with site I and orbital μ as

$$q_{I\mu} = \sum_{J\nu} \rho^{I\mu J\nu} S_{J\nu I\mu}. \tag{22}$$

A non-zero overlap matrix is responsible for the presence of "bond-charge", which (22) allocates to atomic sites [7]. The total number of electrons on site I is

$$q_I = \sum_{\mu} q_{I\mu}. \tag{23}$$

Although the terms on the right-hand side of (22) may in principle be complex, we can be sure that $q_{\mu I}$ is a real number. This property follows automatically because $q_{I\mu}$ is the diagonal element of a matrix that has to be Hermitian because it is a product of two Hermitian matrices. In tight-binding, atomic orbitals are usually chosen to be real so the overlap matrix and expansion coefficients of $\hat{\rho}$ are also real. The expansion coefficients of $\hat{\rho}$ are then identical to the bond orders and we can write

$$q_{I\mu} = \sum_{Jv} \Theta^{I\mu Jv} S_{JvI\mu}. \tag{24}$$

I will replace the density matrix by the bond order when we are implicitly only interested in real orbitals, or Bloch states constructed from real orbitals.

2.2. The local density of states and the Green function

It follows from (6) that we can think of the weight $w_{nI\mu}$ of eigenstate n on site I in orbital μ, as

$$w_{nI\mu} = \sum_{Jv} C_n^{I\mu} C_n^{Jv*} S_{JvI\mu}. \tag{25}$$

The normalisation condition ensures that each eigenstate is distributed over the sites and orbitals such that

$$\sum_{I\mu} w_{nI\mu} = 1. \tag{26}$$

The weights must be real numbers, for the same mathematical reason as the electron numbers in (22). The total density of states per spin is defined by

$$D(\epsilon) = \sum_n \delta(\epsilon - \epsilon_n), \tag{27}$$

it is therefore logical to define the local, partial density of states per spin associated with site I and orbital μ as

$$D_{I\mu}(\epsilon) = \sum_n w_{nI\mu} \delta(\epsilon - \epsilon_n). \tag{28}$$

In a similar fashion the number of electrons associated with site I and orbital μ is

$$q_{I\mu} = \sum_n f_n w_{nI\mu} = \sum_{Jv} \rho^{JvI\mu} S_{I\mu Jv}, \tag{29}$$

which is the result we obtained previously by a different route.

It turns out to be useful to express the densities of states as well as the expansion coefficients of the density operator in terms of the elements of the Green operator $\widehat{G}$, the inverse of $\epsilon - \widehat{H}$, which is defined by

$$\widehat{G}(\epsilon) = \sum_n |n\rangle \frac{1}{\epsilon - \epsilon_n} \langle n|. \tag{30}$$

Like the density operator, the Green operator can be expressed in the local basis by expanding the state vectors $|n\rangle$:

$$\widehat{G}(\epsilon) = \sum_{nI\mu Jv} |I\mu\rangle \frac{C_n^{I\mu} C_n^{Jv*}}{\epsilon - \epsilon_n} \langle Jv|. \tag{31}$$

The relation (31) tells us that the expansion coefficients of the Green operato, variously referred to as Green functions or Green function matrix elements, are given by

$$G^{I\mu J\nu}(\epsilon) = \sum_n \frac{C_n^{I\mu} C_n^{J\nu*}}{\epsilon - \epsilon_n}. \tag{32}$$

This has poles at the eigenvalues, which of course are real numbers. It is most useful when evaluated just above the real axis at an energy $\epsilon + i\eta$, and taking the limit as $\eta \to 0$. Using the relation

$$\text{Im}\lim_{\eta \to 0} \frac{1}{\epsilon + i\eta - \epsilon_n} = -\pi\delta(\epsilon - \epsilon_n). \tag{33}$$

Applying this result to (32) we find

$$-\frac{1}{\pi} G^{I\mu J\nu}(\epsilon^+) = \sum_n C_n^{I\mu} C_n^{J\nu*} \delta(\epsilon - \epsilon_n). \tag{34}$$

The "+" superfix on ϵ is only a reminder that the real value ϵ has been reached by taking a limit from just above the real axis. Now we compare (34) with the similar expression for the density operator expansion coefficient (14). At zero temperature, the occupancies f_n take the value 2 below the Fermi energy ϵ_F and 0 above, so (14) can be written as

$$\rho^{I\mu J\nu} \equiv 2 \int_{-\infty}^{\epsilon_F} C_n^{I\mu} C_n^{J\nu*} \delta(\epsilon - \epsilon_n)\, d\epsilon. \tag{35}$$

Thus, we can link the Green function and density matrix by

$$\rho^{I\mu J\nu} = -\frac{2}{\pi} \int_{-\infty}^{\epsilon_F} G^{I\mu J\nu}(\epsilon^+)\, d\epsilon. \tag{36}$$

The relationship is useful because of the algorithms that have been devised for calculating the elements of $\widehat{G}(\epsilon)$. Furthermore $\widehat{G}(\epsilon)$ is a useful route to the local density of states per spin $D_{I\mu}(\epsilon)$ on site I in orbital μ. Combining 25,28 and 34:

$$D_{I\mu}(\epsilon) = \sum_{J\nu} -\frac{1}{\pi} \text{Im} G^{I\mu J\nu}(\epsilon^+) S_{J\nu I\mu}. \tag{37}$$

2.3. The one-electron energies

Recall that the wavefunctions ψ_n are eigenfunctions of the Hamiltonian $\widehat{H}$ with eigenvalues ϵ_n. This Hamiltonian operator can be expressed as

$$\widehat{H} = \sum_{n=0}^{\infty} |n\rangle \epsilon_n \langle n|. \tag{38}$$

Now consider the trace of the product $\hat{\rho}\widehat{H}$. Using 11,38 and the completeness and orthogonality relations for the eigenstates:

$$\sum_{n=0}^{\infty} |n\rangle\langle n| = 1; \quad \langle n|m\rangle = \delta_{nm} \tag{39}$$

we have

$$\text{Tr}\hat{\rho}\widehat{H} = \sum_{n=0}^{\infty} f_n \epsilon_n \equiv \int_{-\infty}^{\infty} \epsilon f(\epsilon) D(\epsilon)\, \mathrm{d}\epsilon \equiv \int_{-\infty}^{\infty} \epsilon f(\epsilon) \sum_{I\mu} D_{I\mu}(\epsilon)\, \mathrm{d}\epsilon. \tag{40}$$

This is the total one-electron energy of the system, equivalent as indicated to an integral over the total density of states. In solids, we call it the *band energy* and it contains the most significant structure-dependent part of the total energy. Now let us write the same trace in terms of local orbitals, inserting first (15) for $\hat{\rho}$, and expressing it in terms of bond orders:

$$\text{Tr}\hat{\rho}\widehat{H} = \sum_{n=0}^{\infty} \left\langle n \left| \left\{ \sum_{I\mu J\nu} |I\mu\rangle \Theta^{I\mu J\nu} \langle J\nu|\widehat{H} \right\} \right| n \right\rangle = \sum_{I\mu J\nu} \left\langle J\nu \left| \widehat{H} \sum_{n=0}^{\infty} \right| n \right\rangle \langle n|I\mu\rangle \Theta^{I\mu J\nu} \tag{41}$$

then applying the completeness relation (39):

$$\text{Tr}\hat{\rho}\widehat{H} = \sum_{I\mu J\nu} \Theta^{I\mu J\nu} H_{J\nu I\mu}. \tag{42}$$

This expression for the band energy in terms of the bond orders times Hamiltonian matrix elements, or overlap integrals as the latter are sometimes called, has the basic form of a bond-order potential. It has the range of the Hamiltonian matrix itself, which in tight-binding may span as few as two or three shells of neighbours. These Hamiltonian matrix elements are distance and orientation dependent quantities that may be regarded as parameters in a semi-empirical tight-binding model, to be fitted so as to reproduce the one-electron energy bands in an ab initio calculation.

In spite of its simplicity, expression (42) is not necessarily any easier to compute than (40). It depends for its usefulness on finding ways of approximating the bond orders either numerically or analytically in order to avoid the most computer intensive business of calculating all the wavefunctions. Otherwise for computational purposes we could just as well have used the original expression for the band energy. Besides addressing this briefly (it is dealt with in the subsequent papers), we shall show how the on-site terms in (42) can be eliminated from the model, which is very pleasing, since it is precisely the *intersite* terms that represent a sum of *bond* energies. We therefore define the total bond energy as

$$E^{\text{bond}} = \sum_{I,\mu,J\neq I,\nu} \Theta^{I\mu J\nu} H_{J\nu I\mu}. \tag{43}$$

3. Density functional theory

So far we have considered only the contribution of the energies of occupied one-electron states to the bond energy. We shall need to say something about the rest of the energy that is often treated as its ugly sister because of its lack of elegance and general, well repulsiveness. To do this we shall introduce another concept of central importance, namely the *tight-binding bond model* (TBBM), a model of the binding energy referred to free atoms, which is the key to pulling out of the sum (42) all the on-site terms, leaving only intersite contributions from the band energy to the total energy. It becomes a model of the *cohesive* energy rather than the total energy. This will be a benefit when we come to calculate the forces on atoms by differentiating the energy, because we sidestep the problem of differentiating on-site terms. The TBBM was a development that began with Friedel's approach to

tight-binding theory and was worked out in more detail with the advent of density functional theory [8–12,3].

The following subsections outline the development of the TBBM within the framework of density functional theory.

3.1. Ingredients

The ingredients of the density functional theory (DFT) are as follows. First is the electron density $\rho(\mathbf{r})$, which becomes the ground state density $\rho^{ex}(\mathbf{r})$ when the energy functional of $\rho(\mathbf{r})$ is minimized. The superfix "ex" stands for "exact". For the purpose of constructing models a good approximation to ρ^{ex} is the superposition of atomic charge densities, which we designate ρ^{in} because it is also the input charge density, defined by

$$\rho^{in}(\mathbf{r}) = \sum_I \rho^I(\mathbf{r} - \mathbf{R}_I). \tag{44}$$

For any given density, ρ the Hartree functional is its electrostatic self-energy:

$$E_H[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \tag{45}$$

and the corresponding electrostatic potential is

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'. \tag{46}$$

For DFT the most problematic term is the functional $E_{xc}[\rho]$ that represents exchange and correlation, together with its functional derivative $V_{xc}(\mathbf{r})$ representing the exchange and correlation contribution to the one-electron potential

$$\begin{aligned} E_{xc}[\rho] &= ? \\ V_{xc}[\mathbf{r}] &\equiv \frac{\delta E_{xc}[\rho]}{\delta \rho} = ? \end{aligned} \tag{47}$$

which, as the question marks indicate, are unknown, and indeed in exact DFT may be pathological. The usual approach, called the local density approximation (LDA), is to represent E_{xc} locally as its corresponding value in a uniform electron gas, or as a similar quantity corrected by a low order expansion in the gradients of ρ, the so-called generalized gradient approximation (GGA). Finally, we denote the direct Coulomb interaction between nuclei, or more usually ions, as E_{ZZ}, where

$$E_{ZZ} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \tag{48}$$

Ions provide an external potential to the electrons, which for bare ions is given by

$$V_{ext} = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \tag{49}$$

although more usually the ions would include 'core' electrons and be represented by a pseudopotential. The above are ingredients for an effective potential

$$V_{eff} = V_H + V_{xc} + V_{ext}, \tag{50}$$

which enters the Kohn–Sham Hamiltonian referred to in Section 1:

$$\widehat{H}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}). \tag{51}$$

The Kohn–Sham equation with this Hamiltonian emerges from a few lines of calculus, as a formulation of the variational problem: minimize the energy functional of the density $E[\rho]$ specified by

$$E[\rho] = \text{Tr}\hat{\rho}\widehat{H} + E_{\text{xc}} - \int \rho(\mathbf{r})V_{\text{xc}}(\mathbf{r})\,\mathrm{d}\mathbf{r} - E_{\text{H}} + E_{ZZ}, \tag{52}$$

keeping the number of electrons fixed. I have omitted all the mathematical details, since they are well described in the textbooks, e.g. [13].

3.2. The second-order functional

All tight-binding models, and others besides, can be derived from the following form of this functional, which in principle delivers an energy that is exact to second-order in the deviation of the exact ground state charge density ρ^{ex} from ρ^{in}, namely [14,3]:

$$E^{(2)}[\rho^{\text{in}} + \delta\rho] = \text{Tr}\hat{\rho}\widehat{H}^{\text{in}} + E_{\text{xc}}^{\text{in}} - \int \rho^{\text{in}}(\mathbf{r})V_{\text{xc}}^{\text{in}}(\mathbf{r})\,\mathrm{d}\mathbf{r} - E_{\text{H}}^{\text{in}} + E_{ZZ}$$
$$+ \frac{1}{2}\int C_{\text{in}}(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'. \tag{53}$$

The superscript 'in' on any quantity indicates that it is to be evaluated at $\rho = \rho^{\text{in}}$. The density difference $\delta\rho$ is the small quantity in this expansion:

$$\delta\rho = \rho - \rho^{\text{in}}. \tag{54}$$

The kernel in the second-order term is given by the sum of Coulomb and exchange–correlation contributions:

$$C_{\text{in}}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\Bigg|_{\rho^{\text{in}}}. \tag{55}$$

It is worth drawing attention to a couple of features of this rather remarkable functional. It is derived simply by expanding $E_{\text{xc}}[\rho]$ and V_{xc} in (52) to second-order in $\delta\rho$; the only first-order term is implicit in $\text{Tr}\hat{\rho}\widehat{H}^{\text{in}}$. The functional still has to be minimized with respect to ρ in order to obtain the ground state energy, and once this has been done there are no remaining terms of first-order. The first term is no longer the sum of the occupied eigenvalues, because that honour belongs to $\text{Tr}\rho\widehat{H}$. The Hamiltonian including the contribution of $\delta E^{(2)}/\delta\rho$ is

$$\widehat{H}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\text{in}}(\mathbf{r}) + \delta V_{\text{eff}}(\mathbf{r}), \tag{56}$$

where

$$\delta V_{\text{eff}}(\mathbf{r}) = \int C_{\text{in}}(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}'. \tag{57}$$

Minimization of the functional, achieved by solving the Kohn–Sham equation, still requires self-consistency between ρ, generated from the occupied wavefunctions, and the potential V_{eff}. This is done iteratively, which is always a relatively costly business, even in a model form of the full DFT theory such as the one embodied in tight-binding. The final errors are of third-order in $\delta\rho^{\text{in}} - \delta\rho^{\text{ex}}$. Note that the LDA is equivalent to the assumption that the exchange and correlation part of C_{in} is diagonal in r-space, namely $\mathrm{d}^2 E_{\text{xc}}(\rho(\mathbf{r}))/\mathrm{d}\rho^2$.

We could truncate the expansion in (53) at first-order, by omitting the second line altogether, in which case we reduce it to the so-called Harris–Foulkes functional, which requires no self-consistency between the density and the potential, but simply the solution of the Kohn–Sham equations in the input potential. The error in the resulting total energy would be of second-order in $\delta\rho^{\text{in}} - \delta\rho^{\text{ex}}$, but this may be unacceptably large in practice.

4. Atomic charge neutrality

The further road to bond-order potentials will have to be paved with approximations to produce a model that is sufficiently simple. As a first step, let us characterise the charge transfers that take the free atom densities to the final densities by a single quantity on each atom δq_I and thereby make the approximation:

$$\frac{1}{2} \int C_{\text{in}}(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' \approx \frac{1}{2} \sum_I U_I \delta q_I^2 + \frac{1}{2} \sum_{IJ, I \neq J} U_{IJ} \delta q_I \delta q_J. \tag{58}$$

According to (57) the Hamiltonian is thereby augmented by the potential generated by $\delta\rho$, which is now provided by the point charges described by the set of δq_I. Taking into account the overlap matrix (3) this is

$$H_{I\mu J\nu} = H_{I\mu J\nu}^{\text{in}} + \left(U_I \delta q_I + \sum_{I' \neq I} U_{II'} \delta q_{I'} \right) \delta_{IJ} \delta_{\mu\nu}$$

$$+ \frac{1}{2} \left(U_I \delta q_I + U_J \delta q_J + \sum_{I' \neq I} U_{II'} \delta q_{I'} + \sum_{I' \neq J} U_{JI'} \delta q_{I'} \right) O_{I\mu J\nu}. \tag{59}$$

The role of the on-site potentials U_I is like the well-known Hubbard U, tending to damp the electron transfers onto any site. The intersite U_{IJ} include in principle the Coulomb interactions between sites and the exchange–correlation part of C_{in}. However, these are normally neglected in the BOP methodology, and the assumption is made that the charge transfers are negligible. Perhaps surprisingly, this is not as crude as dropping the second-order terms altogether, rather it includes the second-order terms in the limit that the Hubbard U_I are large enough to suppress the charge transfers. This limit is closer to reality than the opposite limit of neglecting the U_I. In metals it is a good way to model the characteristically efficient screening. Otherwise, it is implicitly assumed if we incorporate within H^{in} some prior knowledge of the charge state of ions and do not permit this to change. The effect is to drive the second-order terms in $\delta q_I \delta q_J$ to zero while maintaining a finite contribution to δV_{eff}:

$$U_I \to \infty \quad \text{while} \quad \delta q_I \to 0 \quad \text{and} \quad U_I q_I \text{ finite.} \tag{60}$$

In a numerical solution, the on-site terms in the Hamiltonian matrix are adjusted in an iterative way so as to maintain

$$\delta q_I = 0. \tag{61}$$

If the starting charge density corresponds to neutral free atoms, the above procedure results in local atomic charge neutrality. Alternatively, it could be more accurate to assume that the solid is initially constructed by superimposing ionic charge densities, at least for some of its components. In that case, there will be a long-ranged pairwise Coulomb interaction between the ions from the terms $-E_{\mathrm{H}}^{\mathrm{in}} + E_{ZZ}$ in the total energy (53).

5. The road to a bond-order potential

Rather than the total energy, it is convenient to work with the *binding* energy relative to free atoms, since some of the atomic quantities will thereby cancel. The result of this approach and the above atomic charge neutrality model is generally called the tight-binding bond model (TBBM) [10]. The total binding energy is defined as the difference in total energies:

$$E_{\mathrm{B}} = E^{\mathrm{tot}} \text{ (condensed matter)} - E^{\mathrm{tot}} \text{ (free atoms)}, \tag{62}$$

where the total energy of the free atoms is given by

$$E^{\mathrm{tot}}(\text{free atoms}) = \sum_I \left\{ \mathrm{Tr}\, \widehat{\rho^I}\, \widehat{H}^I + E_{\mathrm{xc}}^I - \int \rho^I(\mathbf{r}) V_{\mathrm{xc}}^I(\mathbf{r}) \mathrm{d}\mathbf{r} - E_{\mathrm{H}}^I \right\}. \tag{63}$$

The single superscript I refers to the isolated free atoms, which are rigidly superimposed to define an input charge density. This would be used to generate the input effective potential according to (50). However, recall in tight-binding the latter is approximated by a sum of spherically symmetric potentials. Using the definition of the bond energy (43) we find

$$E_{\mathrm{B}} = E^{\mathrm{bond}} + \sum_{I\mu\nu} \left\{ \rho^{I\mu I\nu} H_{I\nu I\mu}^{\mathrm{in}} - \rho_I^{I\mu I\mu} H_{I\mu I\mu}^I \right\} - \sum_I \int \rho^I(\mathbf{r})(V_{\mathrm{eff}}^{\mathrm{in}}(\mathbf{r}) - V_{\mathrm{eff}}^I(\mathbf{r}))\, \mathrm{d}\mathbf{r}$$

$$+ E_{\mathrm{xc}}^{\mathrm{in}} - \sum_I E_{\mathrm{xc}}^I + \sum_{I\neq J} \int \rho^I(\mathbf{r}) V_{\mathrm{ext}}^J(\mathbf{r})\, \mathrm{d}\mathbf{r} + \frac{1}{2} \sum_{I\neq J} \int \rho^I(\mathbf{r}) V_{\mathrm{H}}^J(\mathbf{r})\, \mathrm{d}\mathbf{r} + E_{ZZ}. \tag{64}$$

The second term looks very like the promotion energy of electrons from their free atomic states to the states 'prepared' for bonding. Let us for the moment neglect the inter-orbital off-diagonal elements $H_{I\mu I\nu}^{\mathrm{in}}, \mu \neq \nu$ (crystal field splitting) and make the approximation $H_{I\mu I\mu}^{\mathrm{in}} = H_{I\mu I\mu}^I$ (ignoring Madelung energy). Two terms correcting for these approximations will be introduced later. Nevertheless, we still do not quite have the promotion energy, because $\rho^{I\mu I\mu}$ contains less charge than $\rho_I^{I\mu I\mu}$. In order to conserve the number of electrons in the free atom, $\rho^{I\mu I\mu}$ has to be augmented by the bond charge that can be attributed to atom I, as it is in (22). This bond charge contribution is subtracted from E^{bond} to give what is called the covalent energy E^{cov} [15]:

$$E^{\mathrm{cov}} = \sum_{I\mu J\nu, I\neq J} \Theta^{I\mu J\nu}(H_{J\nu I\mu}^{\mathrm{in}} - O_{J\nu I\mu} H_{I\mu I\mu}^{\mathrm{in}}). \tag{65}$$

The covalent energy is more satisfactory than the bond energy originally defined for the physical reason that it is invariant to a constant shift in the external potential. The bond

energy has this property only if the orbitals are orthogonal. So far then we can replace the first two terms of (64) by $E^{\text{cov}} + E^{\text{prom}}$, where the promotion energy is defined as

$$E^{\text{prom}} = \sum_{I\mu} (q_{I\mu} - \rho_I^{I\mu I\mu}) H_{I\mu I\mu}^I. \tag{66}$$

In doing so the two correction terms need to be considered corresponding to crystal field splitting and Madelung-like energy shifts:

$$E^{\text{cfs}} = \sum_{I\mu v} \rho^{I\mu I v} \left(H_{I v I\mu}^{\text{in}} - \delta_{\mu v} H_{I\mu I\mu}^{\text{in}} \right) \tag{67}$$

and

$$E^{\text{M}q} = \sum_{I\mu} q_{I\mu} \left(H_{I\mu I\mu}^{\text{in}} - H_{I\mu I\mu}^I \right). \tag{68}$$

Neither are treated explicitly in the TBBM but are presumed to be included in the pairwise potentials that are parameterised to represent the rest of the energy. They are discussed further in Refs. [3 and 15]. We expect a strong cancellation between the term $E^{\text{M}q}$ and the second line of Eq. (64). If that cancellation were perfect, the only remaining non-pairwise terms in the binding energy would arise from $E_{\text{xc}}^{\text{in}} - E_{\text{xc}}^I$, for which a pairwise potential description is the lowest order approximation [3,16]. The remaining three terms of (64) are pairwise in nature. If the input charge densities are neutral atoms, the pairwise potentials will be repulsive and of short range, consisting of the direct Coulomb repulsions E_{ZZ} screened by the neutral atomic electron distributions. If the input charge densities are of ions, there will in addition be a set of long-ranged Coulomb attractions and repulsions which we denote by E^{ion}. E^{ion} could also be defined to include the energy needed to create the ions from neutral atoms.

That completes the analysis of the binding energy except for any effects due to unequal numbers of up and down spin electrons. Even if we are treating only paramagnetic materials with this model, the free atoms are often spin polarized and this significantly lowers their energy compared to that of the non-magnetic DFT approach we have been following. Thus to avoid grossly overestimating the magnitude of the binding energy (which is an error made by the LDA) at the very least we should subtract a positive term from E_{B}, to represent the energy lowering of free atoms due to their magnetism. This of course plays no part in the energy of rearranging ions within the condensed state. In ferromagnetic or antiferromagnetic materials, there is term in the energy proportional to the square of the moments, as derived for example in the spirit of the Stoner model by Liu et al. [17]. For completeness we should therefore add a (negative) magnetic energy E^{mag} to the final formula for the binding energy. To summarise, with some reasonable approximations and the definitions discussed in this section, we have derived the formula of the TBBM:

$$E_{\text{B}} = E^{\text{cov}} + E^{\text{prom}} + E^{\text{rep}} + E^{\text{ion}} + E^{\text{mag}}. \tag{69}$$

6. Specifying the parameters of the model

The derivation of (69) makes relatively few assumptions, namely no charge transfers when the atoms move (of which atomic charge neutrality is a special case), and the pairwise description of exchange and correlation in $E_{\text{xc}}^{\text{in}}$. There is considerable freedom in how

to specify the parameters of the model, which is not necessarily hampered by the LDA and may actually contain more physics than standard DFT calculations. However, the freedom comes at the price of taking pains to test the transferability of the generated model. Also, there is no completely general procedure which works for all materials. Broadly speaking, the approaches bifurcate between covalent materials and metals, as we shall see.

The first task in using this formula is to parameterise the Hamiltonian matrix. This is conveniently done by fitting band-structures. Another approach, used for example in [18], is to fit matrix elements that have been calculated with a full DFT code using the full-potential LMTO method in its tight-binding representation [19]. The essential features of tight-binding models are that there should be few orbitals on each site, usually no more than 9, which is a minimum basis of s, p and d orbitals, and that the Hamiltonian matrix should be sparse, meaning that its elements are of short range. The Hamiltonian matrix elements are commonly parameterised as a function of bond-length R with a function using three parameters due to Goodwin et al. [20], or generalised with a fourth parameter by Mrovec et al. [18], namely

$$H_{I\mu J\nu}^{\text{in}}(R) = H_{I\mu J\nu}^{\text{in}}(R_0) \times \left(\frac{R_0}{R}\right)^{n_a} \exp\left\{-n_b\left(\frac{R}{R_c}\right)^{n_c}\right\} \exp\left\{n_b\left(\frac{R_0}{R_c}\right)^{n_c}\right\}, \tag{70}$$

where R_0 is the nearest-neighbour distance. Thus the three-centre integrals are ignored, although recent work has modelled them in a simple way at the price of including further parameters [21]. For the purpose of developing bond-order potentials it is also a great simplification to deal with orthogonal orbitals, whereby the non-orthogonality can also be dealt with approximately by folding it into an effective matrix of orthogonal orbitals, in which the two-centre bond-integrals again become environment dependent [18]. These departures from traditional orthogonal two-centre tight-binding seem to be essential for some quantitative applications, as already suggested by Foulkes [22]. The dependence of the Hamiltonian matrix elements on the direction of the bond is easily dealt with by a rotation of the spherical harmonics following the formulae derived by Slater and Koster [23].

The pairwise term E^{rep} will normally be parameterised by fitting energy versus volume, and perhaps other mechanical properties such as elastic constants, to values calculated with a DFT code, or to experimental data. Fitting to experiment is usually preferable because it allows you to repair inevitable deficiencies of even the highest quality benchmark calculations on solids. Since the transition from bulk to free atoms is a continuous one, and the moments of magnetic materials are sensitive to the structure, it is appropriate to make the term E^{mag} also depend on the coordination of atoms and, at least in magnetic materials, on the structure. The question of how best to deal with magnetism within a simple tight-binding model is still a matter of ongoing research.

7. Efficient calculation of the bond order

I have left until last the matter that is normally given centre stage, namely the task of calculating the bond orders themselves in an efficient manner. The essential task is to calculate the Green function, from which the bond order is evaluated from Eq. (36) or the density of states from Eq. (37). The method of choice depends on the material, in particular whether we are dealing with metallic bonds or the saturated bonds of covalent materials. In the case of metals, an atom-centred approach works best, based on (40) and employing the recursion method, whereas for covalent materials like semiconductors

analytic approximations based on a multi-atom expansion of the bond energy have proved successful. The principles of these approaches are outlined here and more fully in the following papers.

7.1. The recursion method

The recursion method [24–30] was developed in order to calculate the matrix elements of $\widehat{G}$ without the machinery of periodic boundary conditions and k-space. It works primarily although not essentially in an orthogonal basis and is equivalent to the Lanczos algorithm for tridiagonalising a matrix, in this case the Hamiltonian matrix. A starting orbital or state is designated $|0\rangle$ and new states, called recursion orbitals and labelled $|1\rangle, |2\rangle$, etc. are generated recursively by successive application of the Hamiltonian, according to

$$|\widetilde{i+1}\rangle = \widehat{H}|i\rangle - a_i|i\rangle - b_i|i-1\rangle \tag{71}$$

followed by the normalisation of the newly generated state $|\widetilde{i+1}\rangle \rightarrow |i+1\rangle$. The coefficients are given by $b_i^2 = \langle\widetilde{i}|\widetilde{i}\rangle$ and $a_i = \langle i|\widehat{H}|i\rangle$. The result is to generate a set of orthonormal orbitals and an effective Hamiltonian for a one-dimensional chain (see Fig. 1) in which only nearest neighbours, represented by the newly generated orbitals, are coupled by the recursion coefficients. The $\{a_i, b_i\}$ are coefficients in a continued fraction expansion of $\langle 0|\widehat{G}|0\rangle$:

$$G_{00}(\epsilon) = \cfrac{1}{\epsilon - a_0 - \cfrac{b_1^2}{\epsilon - a_1 - \cfrac{b_2^2}{\epsilon - a_2 - \cfrac{b_3^2}{\epsilon - \cdots}}}}. \tag{72}$$

The point of this exercise is to choose $|0\rangle$ as a local orbital on atom I, and to calculate the local density of states from (37), which in an orthogonal basis becomes

$$D_0(\epsilon) = -\frac{1}{\pi}\mathrm{Im}G_{00}(\epsilon^+). \tag{73}$$

From $D_0(\epsilon)$ it is a short step to the bond energy, obtained by subtracting the on-site terms from (40). The success of the method depends on a good way to truncate the continued fraction (in effect, the one dimensional chain) the elements of which diminish in importance down the chain. This has been well studied in the references mentioned previously. Even subtle energy differences between different structures are captured by the first few levels. For example the trend in the energy difference BCC–FCC as a function of band-filling
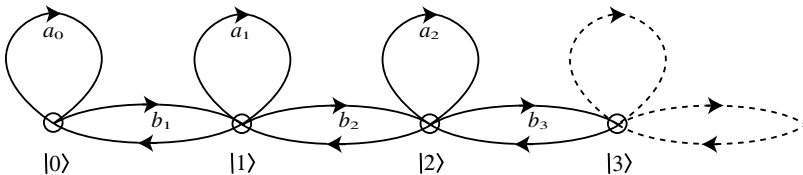

Fig. 1. The recursion chain.

is reproduced with the first two levels, and only three are required to describe the smaller HCP–FCC difference.

There is a related property of the recursion coefficients which is of major importance, namely their relationship to the moments of the corresponding local density of states, where the pth moment is defined by

$$\mu_p = \int_{-\infty}^{\infty} \epsilon^p D_0(\epsilon)\, d\epsilon. \tag{74}$$

An equivalent definition is easily shown to be

$$\mu_p = \langle 0|\widehat{H}^p|0\rangle. \tag{75}$$

Explicit expressions for the first five moments are

$$
\begin{aligned}
\mu_1 &= a_0 \\
\mu_2 &= a_0^2 + b_1^2 \\
\mu_3 &= a_0^3 + 2a_0 b_1^2 + a_1 b_1^2 \\
\mu_4 &= a_0^4 + 3a_0^2 b_1^2 + 2a_0 a_1 b_1^2 + a_1^2 b_1^2 + b_1^4 + b_1^2 b_2^2 \\
\mu_5 &= a_0^5 + 4a_0^3 b_1^2 + 3a_0 b_1^4 + 3a_0^2 a_1 b_1^2 + 2a_0 a_1^2 b_1^2 + 2a_1 b_1^4 \\
&\quad + a_1^3 b_1^2 + 2a_0 b_1^2 b_2^2 + 2a_1 b_1^2 b_2^2 + a_2 b_1^2 b_2^2.
\end{aligned}
\tag{76}
$$

In general, having the coefficients down to a_n, b_n is sufficient to generate $2n+1$ exact moments of the density of states, so that significant detail in the density of states can be recovered from a relatively short continued fraction. The relations (76) can be inverted to express the continued fraction coefficients in terms of the moments, which is useful for some analytical developments of the bond-order potentials to be described next.

7.2. The multi-atom expansion of the energy

The multi-atom energy formula of Tersoff [31] is a well known example of the kind of expression that is desirable from the point of view of including the environment of each bond in some way without requiring a lengthy numerical computation. However, whereas Tersoff's potential was empirically based, and therefore not very transferable to new environments, we expect better transferability from an analytic multi-atom potential based on a quantum mechanical, that is tight-binding, model. Starting from the seminal paper of Pettifor [2] there have been a succession of steps to develop useful analytic expressions for the bond order [32–37]. I will just outline the main principles here, referring to [3] and the following papers for details and the latest developments.

Aoki and Pettifor [32,38] realised the power of starting recursion with the unlikely looking orbital

$$|0^\lambda\rangle = c_i|I\mu\rangle + c_j e^{i\phi}|J\nu\rangle, \tag{77}$$

where the coefficients are real and satisfy

$$c_i^2 + c_j^2 = 1. \tag{78}$$

Defining an auxiliary variable λ by

$$\lambda = \cos\phi \tag{79}$$

gives us the diagonal element

$$G_{00}^{\lambda} = c_i^2 G_{I\mu I\mu} + c_j^2 G_{J\nu J\nu} + 2c_i c_j \lambda G_{I\mu J\nu}. \tag{80}$$

It follows that the off-diagonal elements we are interested in are given by

$$G_{I\mu J\nu} = \frac{1}{2c_i c_j} \frac{\partial G_{00}^{\lambda}}{\partial \lambda}. \tag{81}$$

At first sight this does not look especially promising, because as we have seen, G_{00} can be expressed in terms of recursion coefficients $\{a_i, b_i\}$, but not in any obvious way in terms of λ. However, what can be done is firstly, as we have seen, to express the $\{a_i, b_i\}$ in terms of the moments $\{\mu_p\}$, and then to express the $\{\mu_p\}$ in term of λ. That is all we need to apply the chain rule of differentiation and so to evaluate (81). Furthermore all this can be done at one value of λ; for example $\lambda = 0$ ($\psi = \pi/2$), so the starting orbital is just c_i— $I\mu\rangle$ + ic_j—$J\nu\rangle$.

The derivatives of the moments with respect to λ contain some interesting physics, so it is worth describing that step in a little more detail. If the moments associated with the individual orbitals are $\{\mu_p^{I\mu}\}$ we find

$$\mu_p = \langle 0^{\lambda}|\hat{H}^p|0^{\lambda}\rangle = c_i^2 \mu_p^{I\mu} + c_j^2 \mu_p^{J\nu} + 2c_i c_j \lambda \zeta_{p+1}, \tag{82}$$

and hence

$$\frac{\partial \mu_p}{\partial \lambda} = 2c_i c_j \zeta_{p+1}, \tag{83}$$

where

$$\zeta_{p+1} = \langle J\nu|\hat{H}^p|I\mu\rangle. \tag{84}$$

Hence, a first application of the chain rule to (81) gives us:

$$G_{I\mu J\nu} = \sum_p \frac{\partial G_{00}^{\lambda}}{\partial \mu_p} \zeta_{p+1}. \tag{85}$$

These interference terms ζ_{p+1} therefore have central importance in the theory, because whereas the other terms are additive between sites I and J, the ζ_{p+1} terms carry all the information about how sites I and J are interacting electronically with each other. If we insert the identity operator $\sum_{K\xi}|K\xi\rangle\langle K\xi|$ between each factor $\hat{H}$ in the expression for ζ_{p+1} we can visualise it as a sum over all the paths connecting orbital μ on atom I with orbital ν on atom J that involve p hops from orbital to orbital, each hop being associated with the corresponding Hamiltonian matrix element. The evaluation of interference terms by repeated multiplications of the Hamiltonian matrix is well suited to parallel computation.

The choice of c_i and c_j distinguishes the atom-centred ($c_i = 1$) from the bond-centred ($c_i = c_j$) approaches. The atom-centred approach converges best for unsaturated bonds, as found in metallic systems. For saturated bonds on the other hand, as found in covalent materials, the natural choice of a bond-orbital as starting orbital converges best and lends

itself to constructing analytic models with interference paths of only three or four hops. The form of the analytic bond-order potential depends on making a judicious choice of which paths to include; that is whether 3- 4- or more body terms are required, and how to truncate the sum.

8. Conclusion

In this paper, I have attempted to present a systematic introduction to bond-order potentials and the strategies and approximations required to derive them. Compromises must be made in any of the numerous schemes of total energy calculation for materials science applications, from empirical interatomic potentials to sophisticated first-principles electronic structure theory. BOPs represent a compromise between computational speed and accuracy that strives to retain a sound physical motivation for all the terms involved, and to make transparent approximations as and when necessary. These principles give such simple models the best chance of being transferable, that is able to make predictions outside the range of data to which the model parameters were fitted.

Another particular attraction of bond-order potentials concerns the calculation of forces on atoms. In DFT calculations this is made easy by the Hellmann–Feynman theorem, which says that one only needs to calculate the electrostatic forces on the nuclei due to the self-consistent electron density $\rho(\mathbf{r})$. With an empirical bond-order potential there are no explicit orbitals or wavefunctions in real space, and therefore $\rho(\mathbf{r})$ is not available for this purpose. However, the variational principle that underlies the Hellmann–Feynman theorem can still be exploited when the TBBM energy functional is differentiated; this generates relatively simple formulae for the forces, in which derivatives of charges with respect to position do not appear, but only derivatives of the Hamiltonian and overlap matrix elements, and of the classical interatomic potentials [3].

Examples of applications are given in the following papers.

Acknowledgements

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