

# The Mott–Littleton Method: An Introductory Survey

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This paper aims to provide a broad introduction to the material presented to the conference by surveying the principles of atomistic defect calculations as introduced in the original paper of Mott and Littleton (*Trans. Faraday Soc.*, 1938, **34**, 485) and as developed subsequently. Developments in computational techniques, as represented by the HADES program, have allowed essentially exact representations of particular models to be obtained within the framework of the Mott–Littleton principles. Characteristic defect energies obtained by these methods over the years have provided guidance on the interpretation of observed properties of ionic solids. More recently, the enlargement of the Mott–Littleton principles within the framework of the quasi-harmonic approximation and by reference to the thermodynamics of characteristic defect quantities has allowed the accurate calculation of defect enthalpies, entropies and free volumes as functions of temperature and, if need be, of pressure. It seems likely that such calculations will continue to be valuable in the future as yet more refined and varied models of ionic solids are considered.

## 1. Introduction

This conference has the unusual, but justified, purpose of celebrating the 50th anniversary of the publication of a paper. The occasion is justified for two reasons. First, the paper in question by Mott and Littleton<sup>1</sup> was the first ‘atomistic’ calculation of the energies of lattice defects in any material. By atomistic we mean a calculation dependent upon a knowledge of interatomic forces to obtain the energies (and other properties) of the defects. Secondly, the occasion is justified by the many influential calculations which have been made on the basis of the same general principles which the Mott–Littleton paper itself used.

The purpose of this paper is to provide a broad introduction to the papers which follow by reviewing (i) the principles of the calculations, as they were established originally in the Mott–Littleton (M–L) paper, (ii) how they have been subsequently developed and (iii) how they have been applied within the context of research into the defect solid state. The aim is to enable the reader to see better the significance and limitations of current work. It is not necessary to go into the detailed mathematical expression of these principles to achieve this aim, but if required these can be found in an earlier review by Catlow and Mackrodt<sup>2</sup> and such other sources as are quoted in the text. Since so many applications of the method have been made we shall refer to these mostly *via* the review articles that have been written.

## 2. The Principles of Mott–Littleton Calculations

In the original paper<sup>1</sup> we can discern several principles, which we now list and discuss.

### Interatomic Forces

The representation of interatomic forces or the ‘model’ on which the defect calculation is based is one established by study of the properties of the perfect, or non-defective, solid.

The original calculations were made for one or two alkali halide crystals and the authors adopted the classical Born model of ions bearing integral electric charges. These ions were assumed to interact with Coulomb forces appropriate to these charges and, when close enough for the electronic distributions to overlap, through Born–Mayer overlap repulsions. Parameters in this potential model were chosen so that the perfect solid was in equilibrium at the observed lattice constant and so that it possessed the correct elastic bulk modulus. The point of the principle is essentially the idea of the transferability of interionic forces from one physical state of the compound to another (here perfect solid to imperfect solid). A corollary to the principle is that one does not, without good reason, introduce into defect calculations *ad hoc* features for which there is no evidence from the properties of the perfect solid. Clearly, this cannot be an absolute principle since the basic idea of transferability may not be adequate; as, for example, when dealing with a defect such as an F-centre, where the motion of the F-electron in the field of the anion vacancy would have no analogue in the perfect solid and must be dealt with explicitly and quantum mechanically.<sup>3</sup>

### Defect energies

The original Mott–Littleton calculations were about the energy and structure of point defects. Hence the second principle emerges.

To find defect energies, it is sufficient to minimize the potential energy function  $\Phi$  of the defective static lattice with respect to displacements and moments of the surrounding ions. The difference in the minimum value of  $\Phi$  for different defect ‘states’ of the solid (e.g. perfect solid and solid with a vacancy in it) gives the corresponding defect energy, assumed to be comparable to corresponding experimental energies obtained under thermodynamic conditions of constant temperature and pressure (defect enthalpies). We shall return to this question of the relation of static lattice energies to measured enthalpies later but for the moment we turn to the next M–L principle, which concerns the way in which the minimum of  $\Phi$  is to be found.

### The Minimum of $\Phi$

The task of minimizing  $\Phi$  can be simplified by notionally dividing the defective lattice into two regions; I, containing the defect and a certain number of immediate neighbours, and II, containing the rest of the crystal lattice, which is then described in a continuum approximation. The essential idea of using a continuum solution to yield the displacements and induced moments of the ions in region II ensures that minimization of  $\Phi$  has only to be carried out with respect to the corresponding variables of the ions in region I. It was further assumed that as region I was increased in size the calculated defect energy would quickly converge, although in practice the original calculations were limited to a region I which contained just the vacancy and its first neighbours. This division into I and II is a particularly effective way of dealing with the long-range displacement and polarization fields associated with charged defects. Jost<sup>4</sup> in 1933 had directed attention to the importance of the polarization energy in lowering the energy of defects bearing a net charge. If one may regard an ion vacancy (of net charge  $q$ ) as a spherical cavity of radius  $R$  in a dielectric continuum (of static dielectric constant  $\epsilon_0$ ) then the contribution of the energy of polarization to the defect energy is

$$\frac{-q^2}{2R} \left( 1 - \frac{1}{\epsilon_0} \right), \quad (2.1)$$

which is sizeable and negative. Mott and Littleton took full notice of that and from the

continuum polarization

$$P = \frac{1}{4\pi} \left( 1 - \frac{1}{\epsilon_0} \right) \frac{qr}{r^3} \quad (2.2)$$

inferred individual ion displacements and electronic moments, but they then evaluated the defect energy by summing up the corresponding interactions over the lattice of ions. They did not bother with that part of the ionic displacement field which derived from the fact that the defect is an elastic defect as well as an electrical one.

It is not difficult to see that this omission introduces a relatively small error which decreases rapidly as the size of region I increases. First of all we see that the polarization energy associated with region II is given by (2.1) in which  $R$  is now the outer radius of region I. Likewise, it is not difficult to show that the corresponding elastic energy term in an elastically isotopic solid would amount to

$$\frac{8\pi\mu k^2}{R^3} \quad (2.3)$$

where  $k$  is the elastic strength of the defect (*ca.*  $0.1 r_0^3$  in a NaCl lattice with anion-cation separation of  $r_0$ ) and  $\mu$  the elastic shear modulus. Hence this term quickly decreases as the size of the inner region I increases. Even when region I contains only the nearest neighbours of the defect the elastic term is only *ca.* 10% of the polarization energy (2.1) associated with a charged defect.

### Arrhenius energies

There is perhaps a fourth principle, though a broader one than the other three, to be found. It derives from the values which Mott and Littleton obtained for the Arrhenius energies associated with the ionic conductivity of NaCl, given that this is due to Schottky or, alternatively, Frenkel defects. They showed that this Arrhenius energy would be lower for Schottky than for Frenkel defects and thus concluded that the Schottky mechanism should be dominant. However, their value of 1.5 eV for this Arrhenius energy in the Schottky mechanism was not itself in good agreement with the observed Arrhenius energy governing the ionic conductivity of NaCl of *ca.* 2 eV. The principle is therefore as follows.

The value of these calculations lies in what they suggest about trends and mechanisms rather than in the exact reproduction of experimental values. However, one cannot carry that too far: for how does one know that the calculations are trustworthy unless some experimentally known values are reproduced with good accuracy? Good judgement is required when drawing conclusions in circumstances where inferences from experiment and calculated quantities do not agree. In later years, calculations of defect energies in  $\text{UO}_2$ , in particular, have encountered difficulties of this kind.<sup>5</sup> Nevertheless, the principle is a sensible guide to the choice of calculations.

## 3. Subsequent Developments

In reviewing the work which has derived from the Mott-Littleton paper, it is convenient to distinguish three periods: (i) the primary period, stretching to the late 1960s; (ii) the secondary (or HADES) period, roughly the 1970s; (iii) the tertiary, or quasi-harmonic, period, from *ca.* 1980 onwards. The significance of these designations will emerge from what follows.

### 3.1. The Primary Period

This begins, in effect, almost 10 years after publication of the Mott-Littleton paper since nothing specifically of this kind was done for ionic crystals during the World War II,

although there were the equally pioneering studies of defects in metals by Huntington and Seitz<sup>6</sup> at that time. After the War, however, the notion of lattice defects as a branch of solid-state physics and chemistry emerged, especially in the United States, as a result of the stimulus supplied by Seitz and others.<sup>7</sup> The first post-war Mott-Littleton calculations were done there (on solute-vacancy pairs and anion-cation vacancy pairs) and this activity in turn spread the interest to other countries.

This period then was one in which these calculations were viewed in a wide context of defect solid-state studies. They had their parallels in metals and semiconductors<sup>8</sup> and their conclusions were used in a broad way in the interpretation of ionic transport, radiation effects and mechanical properties. The model substances studied extended gradually from the alkali halides to the alkaline earth halides and to oxides of the alkaline earth metals, the transition metals and uranium. As a result of the increasing availability of computers in this period, groups of compounds could be studied where earlier only one or two at a time had been practical. Nevertheless, the defects studied remained rather simple ones and their symmetry was generally assumed rather than calculated, even at the end of the period.<sup>9</sup>

What of the technical characteristics of the calculations of this period? The models in use were still largely dominated by the idea of starting with the Born model and then fitting the lattice parameter and the compressibility. The dielectric behaviour was generally represented by using either the polarizable point-ion model or the Szigeti deformation-dipole model or shell models.<sup>9</sup> The first class generally overestimated the static dielectric constant when the ionic displacement polarizability was calculated consistently with the Born overlap repulsions obtained from the compressibility. This failing was corrected in the deformation-dipole model by postulating that additional electronic dipoles were generated as a consequence of the ionic overlap arising when the lattice was polarized. In shell models the ions were regarded as composed of a core and a (electronic) shell, the overlap forces arising primarily by the overlap of the shells of neighbouring ions. The assignment of such internal degrees of freedom to the ions also removes the limitations of the polarizable point-ion models by introducing a mechanical coupling between the polarization of an ion (by displacement of the shell relative to the core) and the interaction between overlapping ions.

Shell models eventually became the most favoured not only because they allowed good descriptions of the dielectric properties and lattice dynamics but also because they are unambiguous when there is a change in local lattice coordination, as when a defect is formed. This is essentially because they are models of ions with specified modes of interaction between ions, whereas the deformation-dipole models are really interpretations in terms of the electron distribution between ions, *i.e.* of bonds. They thus become less clear-cut when the local coordination changes. (Indeed this difficulty with bonds remains as a general limitation upon the modelling of defects in covalent materials.)

A general lesson which emerged from the work in this period is the need to match the properties of the discrete, inner region I to those assumed or used for the outer region II. Since the representation of region I is 'atomistic', while that of region II derives directly from a continuum description this means matching the continuum properties corresponding to the atomistic model to the values used in II. Only if this is done can one expect a quick convergence as region I is increased in size. For example, by the same calculation as led to (2.1) we can say that for charged defects and a static dielectric constant  $\epsilon_0$  different in I and II the error in the calculated defect energy for any particular division into I and II will be

$$\text{error} = -\frac{q^2}{2R_1} \left( \frac{1}{\epsilon_0^{\text{I}}} - \frac{1}{\epsilon_0^{\text{II}}} \right), \quad (3.1)$$

which falls only very slowly to zero as  $R_1$  increases and which is worse the greater the mismatch in  $\epsilon_0$ .

Likewise, by the calculation which led to (2.3) a mismatch in elastic properties is less serious, the error in this case falling off like  $R_1^{-3}$ . Many of the early calculations (including those of Mott and Littleton) would therefore have been more accurate if they had fitted the displacement polarizability and hence the Born–Mayer overlap forces to  $\epsilon_0$  rather than to the elastic compressibility. This was shown explicitly by Boswarva for the point-polarizable-ion model.<sup>10</sup> Shell models, by contrast, are sufficiently flexible that they can fit both dielectric and elastic properties (subject to the symmetry limitations associated with the simpler central force versions). In some areas, *e.g.* molecular dynamics, it is still necessary to use very simplified models and here it is important to remember this conclusion. More or less equivalently one can include the defect formation energy among the fitted quantities.

### 3.2. The Secondary (HADES) Period

As the power and availability of large computers increased through the 1960s efficient algorithms and associated subroutines for minimizing functions of many variables were developed, with the Harwell Numerical Analysis Group prominent in this development.<sup>11</sup> This set the scene for the first big advance since the M–L paper, namely Norgett's construction of the HADES general purpose computer program for this type of calculation.<sup>12–14</sup> The advance lay not only in its generality (which covered regions I of arbitrary size in a wide range of cubic lattices and defects), others had implemented such steps previously,<sup>15</sup> but in the use of the speedy and efficient variable-metric minimization algorithm<sup>14</sup> which allowed defects of low symmetry and sizeable regions I to be handled quickly (in times of the order of minutes rather than hours) on the bigger of the computers then available (*e.g.* the IBM 370/75). The computational efficiency of this program allowed calculations to be made with large regions I (several hundreds of ions) and thus explicit tests of the convergence of the M–L method as region I is expanded. In this way it was confirmed that it was now possible to calculate the energies of specified defects in specified models more or less exactly. While earlier calculations suffered from the combined uncertainties over the validity of the physical model and the numerical accuracy of the calculation, it was now possible to separate these.

A further point of practical significance was that HADES was an early example of a 'user-friendly' program, which therefore provided a powerful tool that could be taken up by experimentalists, research students and others without the need for any detailed understanding of its internal operation. This led to a rapid expansion in M–L calculations of defect energies and configurations in ionic solids, which thus became a guide to defect mechanisms in solids.<sup>16</sup>

This expansion and the example established by the HADES program led to a number of associated developments which have further enlarged the subject. These include:

- (1) HADES III for point-defects in non-cubic crystals,<sup>17</sup> with CERBERUS (due to A. N. Cormack) as a convenient preprocessor for handling crystal data input;
- (2) CASCADE (written by M. Leslie) which again treats point defects in non-cubic crystals, and has been optimised for use on vector processing machines, *e.g.* the CRAY computers;
- (3) PLUTO, a program for the calculation of the lattice energy and stability and of elastic and dielectric constants of a specified model;<sup>8</sup>
- (4) TYPHON for the calculation of the lattice dynamical properties of specified potential models;
- (5) MIDAS, a program for studying the structure and energies of surfaces and interfaces in ionic crystals,<sup>19</sup>
- (6) CHAOS, a program based on HADES III for calculating the energies of point defects close to planar interfaces in ionic crystals.<sup>20</sup>



It is clear that both PLUTO and TYPHON have an obvious application to the testing and parameterization of models for use in HADES, while MIDAS and CHAOS represent extensions to surface defects.<sup>21</sup> Analogous extensions to the description of dislocation structure and point-defect dislocation interactions have been made by Puls *et al.*<sup>22</sup> with the program PDINT.

These advances in the techniques of calculation in turn led to an increased effort on the improvement of the lattice potential functions used in these calculations. Although much of this effort was devoted to ways of refining potential functions empirically within the framework of the Born model, another part was concerned with the use of quantum-mechanical calculations of one sort or another to this end. In particular connection with oxides, Mackrodt *et al.*<sup>23</sup> have emphasized the importance of evaluating the interionic potentials in the crystal environment. A compilation of potential functions was made by Stoneham.<sup>24</sup>

### 3.3. Tertiary (Quasi-Harmonic) Period

Although the quasi-harmonic description of the lattice vibrations and the thermodynamic properties of perfect and defective solids has long been used, we here use the term for the period after about 1980 because there then began an expansion of the scope of the calculations which allowed more careful attention to defect properties and their dependence on temperature.

To appreciate the significance of this development let us return to the matter of the relation between the 'energies' calculated, as by the M-L method, in a static lattice and 'energies' obtained from Arrhenius representations of defect concentrations, mobilities, reaction constants, *etc.*, *viz.*

$$P = P_0 \exp(-Q/kT) \quad (3.2)$$

in which  $P$  is the property referred to and  $Q$  is the corresponding Arrhenius or activation energy. The usual methods of analysis of  $P$  by statistical thermodynamics (which is also the basis of the usual transition-state theory of mobilities) then disclose that in these applications, or at least in the simpler of them, the quantity  $Q = \partial(\ln P)/\partial(1/kT)$  has the nature of an enthalpy. Insofar as the property  $P$  is associated with a change in the defect condition of the crystal (*e.g.* when  $P$  is the defect concentration the change in defect condition corresponds to the formation of the defect) the quantity  $Q$  is the corresponding change in enthalpy at constant temperature and pressure. The second of the M-L principles set out in section 2 is then equivalent to the assertion that this enthalpy can be adequately approximated by the corresponding static lattice potential energy at  $T = 0$ .

The quasi-harmonic approximation throws light on this. First, it shows that the difference in potential energies  $\Phi_2(V) - \Phi_1(V)$  for the change in defect state of the solid  $1 \rightarrow 2$  at constant volume (or more generally at constant lattice parameter), and at high temperatures where classical equipartition holds among the vibrational modes, is equal to the corresponding internal energy change at constant  $(V, T)$ , *i.e.*

$$u_V = \Phi_2(V) - \Phi_1(V) \quad (3.3)$$

Likewise, there is a corresponding entropy change

$$s_V = -k \left( \sum_{j'} \ln \omega_{j'}^{(2)} - \sum_j \ln \omega_j^{(1)} \right) \quad (3.4)$$

in which  $\omega_j^{(1)}$  are the vibrational frequencies of the lattice in defect state 1; and similarly for state 2. These results have been known for a long while, but, to avoid possible misunderstanding, we emphasize that they do not imply that the change in defect state of the crystal is described in the harmonic approximation, but only that the lattice vibrations in any particular defect state are describable in such an approximation.

The second observation is that there is a set of simple relations between these quantities for changes at constant volume and the corresponding quantities for the same process as would be measured experimentally at constant pressure. These relations have been derived over the years by various authors<sup>25</sup> and are as follows

$$g_P = f_V, \quad (3.5a)$$

$$h_P = u_V + T \frac{\beta_P}{\kappa_T} v_P, \quad (3.5b)$$

$$s_P = s_V + \frac{\beta_P}{\kappa_T} v_P, \quad (3.5c)$$

$$v_P = -\kappa_T V (\partial f_V / \partial V)_T. \quad (3.5d)$$

Here  $g_P$ ,  $h_P$ ,  $s_P$  and  $v_P$  are, respectively, the Gibbs free energy, the enthalpy, the entropy and the free volume for the change in defect state at constant  $T$  and  $P$ . Likewise,  $f_V$ ,  $u_V$  and  $s_V$  are, respectively, the Helmholtz free energy, internal energy and entropy for the same change at constant  $T$  and  $V$  (or constant lattice parameter if the total number of lattice sites varies during the change). The quantity  $\beta_P$  is the thermal expansion coefficient and  $\kappa_T$  is the isothermal compressibility. The combination of these relations with eqn (3.3) and (3.4) thus shows how to calculate quantities that may be compared directly with experimentally determined quantities.

The original M-L paper assumed that  $h_P(T) = u_V(0)$ , but this requires additional simplifications.<sup>26</sup> If we do not want to be limited in these ways then the implications are twofold. First, we shall need to calculate  $s_V$  as well as  $u_V$  in order to get  $f_V$ , and thus  $v_P$ ,  $g_P$ ,  $h_P$  and  $s_P$ . Furthermore, these quantities should be obtained as functions of temperature.

Secondly, because in the quasi-harmonic approximation the temperature dependence of  $u_V$  and  $s_V$  enters solely through the temperature dependence of the lattice parameter, the potential model employed should be further tested by calculating the temperature variation of the lattice parameter of the perfect crystal in the quasi-harmonic approximation and verifying that this agrees with the observed variation. Furthermore, in view of the importance of the static dielectric constant,  $\epsilon_0$ , the temperature variation of this too should be checked.

Clearly, these extensions imply a substantial increase in effort, but in the last few years they have been demonstrated to be feasible. The key step is the calculation of  $s_V$ . Research in recent years has led to the construction by Harding<sup>27</sup> of the SHEOL program for the calculation of this quantity to stand alongside HADES for the calculation of  $u_V$ . The variations of lattice parameter, and of the elastic and dielectric constants with temperature are obtainable from the PLUTO code already mentioned. With all these tools it is then practicable to develop models and to test them within the framework of the quasi-harmonic approximation and then to calculate their defect properties as a function of temperature. A clear illustration of the practicability of such a scheme is provided by the study of Frenkel defects in  $\text{CaF}_2$  by Harding.<sup>28</sup>

#### 4. The Achievements

The above remarks have largely centred on the nature and reliability of the calculations, and on the details of the relations between calculated and experimentally determined quantities. However, we should recognize the contributions which calculations of the M-L type have made to the science of defects in solids. Even in the primary period when the calculated energies were uncertain in several ways, the calculations of characteristic energies of a range of vacancy and interstitial defects lent general support, as well as particular interpretations, to the experimental study of defects and associated

processes in ionic crystals.<sup>9,16</sup> In turn this added to the general confidence in the defect models employed in the interpretation of properties other than those envisaged in the course of these particular calculations, for example the interpretation of certain electrical and mechanical properties in terms of charged dislocations.<sup>29</sup> As confidence in the calculations grew, insights into more complex defects were obtained, in particular into various unexpected structures of low symmetry.<sup>30</sup> Since it is now possible to obtain the characteristic thermodynamic quantities as functions of temperature<sup>28</sup> there is every reason to suppose that additional insights into defect properties and associated processes will be obtained in the immediate future.<sup>31</sup>

## 5. Conclusion

In the course of this brief survey we have seen that the seed represented by the Mott-Littleton paper has grown into a healthy and fertile tree. It seems likely that it will survive for many years yet, for the present methods of calculation (*i.e.* those taking advantage of the quasi-harmonic approximation) are likely to remain competitive in computer time and cost. Foremost among the alternatives is the method of molecular dynamics, but the representation of ionic polarizability still imposes a great burden on such computations. Even with advances in computing power it seems inevitable that the M-L type of calculation will maintain its position by its ability to handle precisely yet more detailed models of interionic interactions. The consideration of electronic quadrupolar terms in the transition-metal oxides<sup>31</sup> is one example of this. Others will undoubtedly be provided by attempts to deal consistently with those 'open-shell' defects requiring a quantum-mechanical description of the defect itself (*e.g.* the F-centre) by grafting such a description of region I onto a M-L description of region II. In these circumstances it seems probable that detailed predictions will continue to be made by the M-L method as long as its general principles are seen to remain valid. The role of the more fundamental yet far more costly molecular dynamics computations must surely be to confirm or to modify those general principles.

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